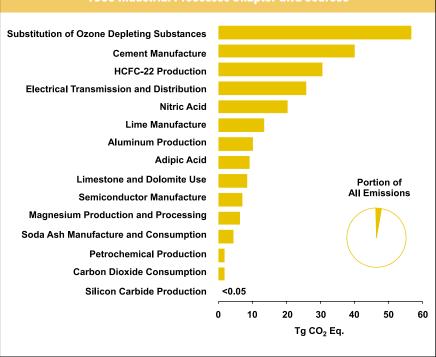
# 3. Industrial Processes

reenhouse gas emissions are produced as a by-product of various non-energy-related industrial activities. That is, these emissions are produced from an industrial process itself and are not directly a result of energy consumed during the process. For example, raw materials can be chemically transformed from one state to another. This transformation can result in the release of greenhouse gases such as carbon dioxide  $(CO_2)$ , methane  $(CH_4)$ , or nitrous oxide  $(N_2O)$ . The processes addressed in this chapter include cement production, lime manufacture, limestone and dolomite use (e.g., flux stone, flue gas desulfurization, and glass manufacturing), soda ash production and use,  $CO_2$  consumption, iron and steel production, ammonia manufacture, ferroalloy production, aluminum production, petrochemical production, silicon carbide production, adipic acid production, and nitric acid production (see Figure 3-1).

In addition to the three greenhouse gases listed above, there are also industrial sources of several classes of man-made fluorinated compounds called hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulfur hexafluoride (SF<sub>6</sub>). The present contribution of these gases to the radiative forcing effect of all anthropogenic greenhouse gases is small; however, because of their extremely long lifetimes, they will continue to accumulate in the atmosphere as long as emissions continue. Sulfur hexafluoride, itself, is the most potent greenhouse gas the IPCC has ever evaluated. Usage of these gases, especially HFCs, is growing rapidly as they are the

Figure 3-1
1999 Industrial Processes Chapter GHG Sources



<sup>&</sup>lt;sup>1</sup> Carbon dioxide emissions from iron and steel production, ammonia manufacture, ferroalloy production, and aluminum production are accounted for in the Energy chapter under Fossil Fuel Combustion of industrial coking coal, natural gas, and petroleum coke.

primary substitutes for ozone depleting substances (ODSs), which are being phased-out under the *Montreal Protocol on Substances that Deplete the Ozone Layer*. In addition to ODS substitutes, HFCs, PFCs, and other fluorinated compounds are employed and emitted by a number of other industrial sources in the United States. These industries include aluminum production, HCFC-22 production, semiconductor manufacture, electric power transmission and distribution, and magnesium metal production and processing.

In 1999, industrial processes generated emissions of 234.0 Tg CO<sub>2</sub> Eq., or 3.5 percent of total U.S. greenhouse gas emissions. Carbon dioxide emissions from all industrial processes were 67.4 Tg CO<sub>2</sub> Eq. (67,401 Gg) in the same year. This amount accounted for only 1.2 percent of national CO<sub>2</sub> emissions. Methane emissions from petrochemical and silicon carbide production resulted in emissions of approximately 1.7 Tg CO<sub>2</sub> Eq. (80 Gg) in 1999, which was less than 1 percent of U.S. CH₄ emissions. Nitrous oxide emissions from adipic acid and nitric acid production were 29.2 Tg CO<sub>2</sub> Eq. (94 Gg) in 1999, or 6.8 percent of total U.S. N<sub>2</sub>O emissions. In the same year, combined emissions of HFCs, PFCs and SF<sub>6</sub> totaled 135.7 Tg CO<sub>2</sub> Eq. Overall, emissions from industrial processes increased by 33 percent from 1990 to 1999, which was the result of increases in emissions from several industrial processes—the largest being substitutes for ozone depleting substances—which was offset by decreases in emissions from adipic acid production, aluminum production, and production of HCFC-22.

Emission estimates are presented in this chapter for several industrial processes that are actually accounted for within the Energy chapter. Although process-related  ${\rm CO}_2$  emissions from iron and steel production, ammonia manufacture, ferroalloy production, and aluminum production are not the result of the combustion of fossil fuels for energy, their associated emissions are captured in the fuel data for industrial coking coal, natural gas,

industrial coking coal, and petroleum coke, respectively. Consequently, if all emissions were attributed to their appropriate chapter, then emissions from energy would decrease by approximately  $105.0 \, \mathrm{Tg} \, \mathrm{CO}_2 \, \mathrm{Eq}$ . in 1999, and industrial process emissions would increase by the same amount.

Greenhouse gases are also emitted from a number of industrial processes not addressed in this chapter. For example, caprolactam—a chemical feedstock for the manufacture of nylon 6,6—and urea production are believed to be industrial sources of N<sub>2</sub>O emissions. However, emissions for these and other sources have not been estimated at this time due to a lack of information on the emission processes, manufacturing data, or both. As more information becomes available, emission estimates for these processes will be calculated and included in future greenhouse gas emission inventories, although their contribution is expected to be small.<sup>2</sup>

The general method employed to estimate emissions for industrial processes, as recommended by the Intergovernmental Panel on Climate Change (IPCC), involves multiplying production data for each process by an emission factor per unit of production. The emission factors used were either derived using calculations that assume precise and efficient chemical reactions or were based upon empirical data in published references. As a result, uncertainties in the emission coefficients can be attributed to, among other things, inefficiencies in the chemical reactions associated with each production process or to the use of empirically derived emission factors that are biased and, therefore, may not represent U.S. national averages. Additional sources of uncertainty specific to an individual source category are discussed in each section.

Table 3-1 summarizes emissions for the Industrial Processes chapter in units of teragrams of carbon dioxide equivalents (Tg CO<sub>2</sub> Eq.), while unweighted gas emissions in gigagrams (Gg) are provided in Table 3-2.

<sup>&</sup>lt;sup>2</sup> See Annex P for a discussion of emission sources excluded.

Table 3-1: Emissions from Industrial Processes (Tg CO<sub>2</sub> Eq.)

Gas/Source	1990	1995	1996	1997	1998	1999
CO,	54.6	61.9	63.3	66.1	67.0	67.4
Cement Manufacture	33.3	36.8	37.1	38.3	39.2	39.9
Lime Manufacture	11.2	12.8	13.5	13.7	13.9	13.4
Limestone and Dolomite Use	5.1	7.0	7.3	8.3	8.1	8.3
Soda Ash Manufacture and Consumption	4.1	4.3	4.3	4.4	4.3	4.2
Carbon Dioxide Consumption	0.8	1.0	1.1	1.3	1.4	1.6
Iron and Steel Production*	87.6	81.4	79.0	79.4	77.1	71.8
Ammonia Manufacture*	23.1	23.7	24.4	24.3	25.1	25.8
Ferroalloy Production*	1.8	1.6	1.7	1.8	1.8	1.8
Aluminum Production*	6.0	5.0	5.3	5.3	5.5	5.6
CH <sub>4</sub>	1.2	1.5	1.6	1.6	1.6	1.7
Petrochemical Production	1.2	1.5	1.6	1.6	1.6	1.7
Silicon Carbide Production	+	+	+	+	+	+
$N_2O$	36.1	40.2	41.5	38.3	28.1	29.2
Nitric Acid Production	17.8	19.9	20.7	21.2	20.9	20.2
Adipic Acid Production	18.3	20.3	20.8	17.1	7.3	9.0
HFCs, PFCs, and SF <sub>6</sub>	83.9	99.0	115.1	123.3	138.6	135.7
Substitution of Ozone Depleting Substances	0.9	24.0	34.0	42.1	49.6	56.7
HCFC-22 Production	34.8	27.1	31.2	30.1	40.0	30.4
Electrical Transmission and Distribution	20.5	25.7	25.7	25.7	25.7	25.7
Aluminum Production	19.3	11.2	11.6	10.8	10.1	10.0
Semiconductor Manufacture	2.9	5.5	7.0	7.0	6.8	6.8
Magnesium Production and Processing	5.5	5.5	5.6	7.5	6.3	6.1
Total	175.8	202.7	221.5	229.3	235.3	234.0

<sup>+</sup> Does not exceed 0.05 Tg CO<sub>2</sub> Eq.

# **Cement Manufacture**

Cement manufacture is an energy and raw material intensive process resulting in the generation of carbon dioxide (CO<sub>2</sub>) from both the energy consumed in making the cement and the chemical process itself.<sup>3</sup> Cement production has accounted for about 2.4 percent of total global industrial and energy-related CO<sub>2</sub> emissions (IPCC 1996), and the United States is the world's third largest cement producer. Cement is manufactured in almost every State and is used in all of them. Carbon dioxide emitted from the chemical process of cement production represents one of the largest sources of industrial CO<sub>2</sub> emissions in the United States.

During the cement production process, calcium carbonate (CaCO<sub>3</sub>) is heated in a cement kiln at a temperature of about 1,300°C (2,400°F) to form lime (i.e., calcium oxide or CaO) and CO<sub>2</sub>. This process is known as

calcination or calcining. Next, the lime is combined with silica-containing materials to produce clinker (an intermediate product), with the earlier by-product CO<sub>2</sub> being released to the atmosphere. The clinker is then allowed to cool, mixed with a small amount of gypsum, and used to make Portland cement. The production of masonry cement from Portland cement requires additional lime and, thus, results in additional CO<sub>2</sub> emissions. However, this additional lime is already accounted for in the Lime Manufacture source category in this chapter; therefore, the additional emissions from making masonry cement from clinker are not counted in this source category's total. They are presented here for informational purposes only.

In 1999, U.S. clinker production—including Puerto Rico—totaled 77,152 thousand metric tons, and U.S. masonry cement production was estimated to be 4,127 thousand metric tons (USGS 2000). The resulting emissions of

<sup>\*</sup> Emissions from these sources are accounted for in the Energy chapter and are not included in the Industrial Processes totals. Note: Totals may not sum due to independent rounding.

 $<sup>^3</sup>$  The  $\mathrm{CO}_2$  emissions related to the consumption of energy for cement manufacture are accounted for under  $\mathrm{CO}_2$  from Fossil Fuel Combustion in the Energy chapter.

Table 3-2: Emissions from Industrial Processes (Gg)

Gas/Source 199	0	1995	1996	1997	1998	1999
CO <sub>2</sub> 54,57	7	61,917	63,293	66,063	66,984	67,401
Čement Manufacture 33,27	8	36,847	37,079	38,323	39,218	39,896
Lime Manufacture 11,23	8	12,805	13,495	13,685	13,914	13,426
Limestone and Dolomite Use 5,11	7	6,987	7,305	8,327	8,114	8,290
Soda Ash Manufacture and Consumption 4,14	4	4,309	4,273	4,434	4,325	4,217
Carbon Dioxide Consumption 80	0	968	1,140	1,294	1,413	1,572
Iron and Steel Production <sup>a</sup> 87,60	0	81,440	79,040	79,360	77,120	71,840
Ammonia Manufacture <sup>a</sup> 23,13	8	23,682	24,390	24,346	25,141	25,799
Ferroalloy Production <sup>a</sup> 1,80	9	1,625	1,695	1,789	1,793	1,771
Aluminum Production <sup>a</sup> 5,95	1	4,961	5,258	5,296	5,458	5,555
CH, 5	7	72	76	77	78	80
Petrochemical Production 5	6	72	75	77	77	79
Silicon Carbide Production	1	1	1	1	1	1
$N_2O$	7	130	134	124	91	94
Nitric Acid Production 5	8	64	67	68	67	65
Adipic Acid Production 5	9	66	67	55	23	29
HFCs, PFCs, and SF <sub>6</sub>	M	M	M	M	M	M
HCFC-22 Production <sup>b</sup>	3	2	3	3	3	3
Electrical Transmission and Distribution <sup>c</sup>	1	1	1	1	1	1
Substitution of Ozone Depleting Substances	M	M	M	M	M	M
Aluminum Production	M	M	M	M	M	M
Semiconductor Manufacture	M	M	M	M	M	M
Magnesium Production and Processing <sup>c</sup>	+	+	+	+	+	+

<sup>+</sup> Does not exceed 0.5 Gg

Note: Totals may not sum due to independent rounding.

 ${
m CO_2}$  from clinker production were estimated to be 39.9 Tg  ${
m CO_2}$  Eq. (39,896 Gg) (see Table 3-3). Emissions from masonry production from clinker raw material were estimated to be 0.09 Tg  ${
m CO_2}$  Eq. (93 Gg) in 1999, but again are accounted for under Lime Manufacture.

After falling in 1991 by 2 percent from 1990 levels, cement production emissions have grown every year since. Overall, from 1990 to 1999, emissions increased by 20 percent. In 1999, output by cement plants increased 2 percent over 1998, to 77,152 thousand metric tons. Cement is a critical component of the construction industry; therefore, the availability of public construction funding, as well as overall economic growth, have had considerable influence on cement production.

Table 3-3: CO<sub>2</sub> Emissions from Cement Production\*

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	33.3	33,278
1995	36.8	36,847
1996	37.1	37,079
1997	38.3	38,323
1998	39.2	39,218
1999	39.9	39,896

<sup>\*</sup> Totals exclude CO<sub>2</sub> emissions from making masonry cement from clinker, which are accounted for under Lime Manufacture.

M (Mixture of gases)

<sup>&</sup>lt;sup>a</sup> Emissions from these sources are accounted for in the Energy chapter and are not included in the Industrial Processes totals.

b HFC-23 emitted

<sup>&</sup>lt;sup>c</sup> SF<sub>6</sub> emitted

Carbon dioxide emissions from cement manufacture are created by the chemical reaction of carbon-containing minerals (i.e., calcining limestone). While in the kiln, limestone is broken down into CO<sub>2</sub> and lime with the CO<sub>2</sub> released to the atmosphere. The quantity of the CO<sub>2</sub> emitted during cement production is directly proportional to the lime content of the clinker. During calcination, each mole of CaCO<sub>3</sub> (i.e., limestone) heated in the clinker kiln forms one mole of lime (CaO) and one mole of CO<sub>2</sub>:

$$CaCO_3 + heat \rightarrow CaO + CO_2$$

Carbon dioxide emissions were estimated by applying an emission factor, in tons of  $\mathrm{CO}_2$  released per ton of clinker produced, to the total amount of clinker produced. The emission factor used in this analysis is the product of the average lime fraction for clinker of 64.6 percent (IPCC 2000) and a constant reflecting the mass of  $\mathrm{CO}_2$  released per unit of lime. This calculation yields an emission factor of 0.507 tons of  $\mathrm{CO}_2$  per ton of clinker produced, which was determined as follows:

$$EF_{Clinker} = 0.646 \text{ CaO} \times \left[ \frac{44.01 \text{ g/mole CO}_2}{56.08 \text{ g/mole CaO}} \right] = 0.507 \text{ tons CO}_2/\text{ton clinker}$$

During clinker production, some of the clinker precursor materials remain in the kiln as non-calcinated, partially calcinated, or fully calcinated cement kiln dust (CKD). The emissions attributable to the calcinated portion of the CKD are not accounted for by the clinker emission factor. The IPCC recommends that these additional CKD CO<sub>2</sub> emissions should be estimated as 2 percent of the CO<sub>2</sub> emissions calculated from clinker production. Total cement production emissions were calculated by adding the emissions from clinker production to the emissions assigned to CKD (IPCC 2000).

Masonry cement requires additional lime over and above the lime used in clinker production. In particular, non-plasticizer additives such as lime, slag, and shale are added to the cement, increasing its weight by approximately 5 percent. Lime accounts for approximately 60 percent of this added weight. Thus, the additional lime is equivalent to roughly 2.86 percent of the starting amount of the product, since:

$$0.6 \times 0.05/(1 + 0.05) = 2.86\%$$

An emission factor for this added lime can then be calculated by multiplying this percentage (2.86 percent) by the molecular weight ratio of  ${\rm CO_2}$  to  ${\rm CaO}$  (0.785) to yield 0.0224 metric tons of additional  ${\rm CO_2}$  emitted for every metric ton of masonry cement produced.

As previously mentioned, the  $\mathrm{CO}_2$  emissions from the additional lime added during masonry cement production are accounted for in the section on  $\mathrm{CO}_2$  emissions from Lime Manufacture. Thus, these emissions were estimated in this chapter for informational purposes only, and are not included in the cement emission totals.

### **Data Sources**

The activity data for clinker and masonry cement production (see Table 3-4) were obtained from U.S. Geological Survey (USGS 1992, 1995a, 1995b, 1996, 1997, 1998, 1999, 2000). The data were compiled by USGS through questionnaires sent to domestic clinker and cement manufacturing plants. The 1999 value for masonry cement production was calculated by applying the average annual growth rate for 1995 through 1998 to the reported 1998 masonry cement production value.

# **Uncertainty**

The uncertainties contained in these estimates are primarily due to uncertainties in the lime content of clinker, in the amount of lime added to masonry cement, and in the percentage of CKD recycled inside the clinker kiln. The lime content of clinker varies from 64 to 66 percent. CKD loss can range from 1.5 to 8 percent depending upon plant specifications. Additionally, some amount of  $\mathrm{CO}_2$  is

Table 3-4: Cement Production (Gg)

Year	Clinker	Masonry
1990	64,355	3,209
1991	62,918	2,856
1992	63,415	3,093
1993	66,957	2,975
1994	69,786	3,283
1995	71,257	3,603
1996	71,706	3,469
1997	74,112	3,634
1998	75,842	3,989
1999	77,152	4,127

reabsorbed when the cement is used for construction. As cement reacts with water, alkaline substances such as calcium hydroxide are formed. During this curing process, these compounds may react with  $\mathrm{CO}_2$  in the atmosphere to create calcium carbonate. This reaction only occurs in roughly the outer 0.2 inches of surface area. Because the amount of  $\mathrm{CO}_2$  reabsorbed is thought to be minimal, it was not estimated.

# **Lime Manufacture**

Lime is an important manufactured product with many industrial, chemical, and environmental applications. Its major uses are in steel making, flue gas desulfurization (FGD) at coal-fired electric power plants, construction, pulp and paper manufacturing, and water purification. Lime has historically ranked fifth in total production of all chemicals in the United States. For U.S. operations, the term "lime" actually refers to a variety of chemical compounds. These include calcium oxide (CaO), or high-calcium quicklime; calcium hydroxide (Ca(OH)<sub>2</sub>), or hydrated lime; dolomitic quicklime ([CaO•MgO]); and dolomitic hydrate ([Ca(OH)<sub>2</sub>•MgO] or [Ca(OH)<sub>2</sub>•Mg(OH)<sub>2</sub>]).

Lime production involves three main processes: stone preparation, calcination, and hydration. Carbon dioxide is generated during the calcination stage, when limestone—mostly calcium carbonate (CaCO<sub>3</sub>)—is roasted at high temperatures in a kiln to produce CaO and

Table 3-5: Net CO<sub>2</sub> Emissions from Lime Manufacture

Year	Tg CO <sub>2</sub> Eq.
1990	11.2
1995	12.8
1996	13.5
1997	13.7
1998	13.9
1999	13.4

CO<sub>2</sub>. The CO<sub>2</sub> is driven off as a gas and is normally emitted to the atmosphere. Some of the CO<sub>2</sub> generated during the production process, however, is recovered at some facilities for use in sugar refining and precipitated calcium carbonate (PCC)<sup>4</sup> production. It is also important to note that, for certain applications, lime reabsorbs CO<sub>2</sub> during use (see Uncertainty, below).

Lime production in the United States—including Puerto Rico—was reported to be 19,618 thousand metric tons in 1999 (USGS 2000). This resulted in estimated  $\rm CO_2$  emissions of 13.4 Tg  $\rm CO_2$  Eq. (13,426 Gg) (see Table 3-5 and Table 3-6).

At the turn of the century, over 80 percent of lime consumed in the United States went for construction uses. The contemporary quicklime market is distributed across its four end-use categories as follows: metallurgical uses, 39 percent; chemical and industrial uses, 26 percent; environmental uses, 24 percent; and construction uses, 11 percent. Construction end-uses are still important to the hydrated lime market, accounting for 54 percent of consumption. However, hydrated lime constitutes only 10 percent of the total lime market.

Lime production in 1999 declined 2 percent from 1998, the first drop in annual production since 1991. Overall, from 1990 to 1999, lime production increased by 24 percent. The increase in production is attributed in part to growth in demand for environmental applications, especially flue gas desulfurization technologies. In 1993,

Table 3-6: CO<sub>2</sub> Emissions from Lime Manufacture (Gg)

Year	Potential	Recovered*	Net Emissions
1990	11,731	(493)	11,238
1995	13,702	(896)	12,805
1996	14,348	(852)	13,495
1997	14,649	(964)	13,685
1998	14,975	(1,061)	13,914
1999	14,609	(1,183)	13,426

<sup>\*</sup> For sugar refining and precipitated calcium carbonate production.

Note: Totals may not sum due to independent rounding.

<sup>&</sup>lt;sup>4</sup> Precipitated calcium carbonate is a specialty filler used in premium-quality coated and uncoated papers.

the U.S. Environmental Protection Agency (EPA) completed regulations under the Clean Air Act capping sulfur dioxide (SO<sub>2</sub>) emissions from electric utilities. Lime scrubbers' high efficiencies and increasing affordability have allowed the FGD end-use to expand from 10 percent of total lime consumption in 1990 to 14 percent in 1999 (USGS 1992, 2000).

# Methodology

During the calcination stage of lime manufacture,  $\mathrm{CO}_2$  is driven off as a gas and normally exits the system with the stack gas. To calculate emissions, the amounts of high-calcium and dolomitic lime produced were multiplied by their respective emission factors. The emission factor is the product of a constant reflecting the mass of  $\mathrm{CO}_2$  released per unit of lime and the average calcium plus magnesium oxide ( $\mathrm{CaO} + \mathrm{MgO}$ ) content for lime (95 percent for both types of lime). The emission factors were calculated as follows:

For high-calcium lime:  $[(44.01 \text{ g/mole CO}_2) \div (56.08 \text{ g/mole CaO})] \times (0.95 \text{ CaO/lime}) = 0.75 \text{ g CO}_2/\text{g lime}$ 

For dolomitic lime:  $[(88.02 \text{ g/mole CO}_2) \div (97.01 \text{ g/mole CaO})] \times (0.95 \text{ CaO/lime}) = 0.86 \text{ g CO}_2/\text{g lime}$ 

Production is adjusted to remove the mass of water found in hydrated lime, using the midpoint of default ranges provided by the *IPCC Good Practice Guidance* (IPCC 2000). These factors set the water content to 27 percent for high-calcium hydrated lime, and 24 percent for dolomitic hydrated lime.

Lime production in the United States was 19,618 thousand metric tons in 1999 (USGS 2000), resulting in potential CO<sub>2</sub> emissions of 14,609 Gg. Some of the CO<sub>2</sub> generated during the production process, however, was recovered for use in sugar refining and precipitated calcium carbonate (PCC) production. Combined lime manufacture by these producers was 1,983 thousand metric tons in 1999, generating 1.5 Tg of CO<sub>2</sub>. It was assumed that approximately 80 percent of the CO<sub>2</sub> involved in sugar refining and PCC was recovered.

#### **Data Sources**

The activity data for lime manufacture and lime consumption by sugar refining and precipitated calcium carbonate (PCC) for 1990 through 1992 (see Table 3-7) were

obtained from USGS (1992, 1994, 1995, 1996, 1997, 1998, 1999, 2000). The CaO and CaO•MgO contents of lime were obtained from the *IPCC Good Practice Guidance* (IPCC 2000). Since data for the individual lime types was not provided prior to 1997, total lime production for 1990 through 1996 was allocated according to the 1997 distribution. For lime consumption, it was assumed that 100 percent was high-calcium based on communication with the National Lime Association (Males 2001).

## **Uncertainty**

Uncertainties in the emission estimate can be attributed to slight differences in the chemical composition of these products. Although the methodology accounts for various formulations of lime, it does not account for the trace impurities found in lime, such as iron oxide,

Table 3-7: Lime Production and Lime Use for Sugar Refining and PCC (Thousand Metric Tons)

Year	High-Calcium Production <sup>2</sup>	Dolomite Production <sup>a,b</sup>	Use
1990	12,941	2,901	826
1991	12,833	2,845	964
1992	13,300	2,932	1,023
1993	13,734	3,031	1,279
1994	14,268	3,122	1,374
1995	15,185	3,313	1,503
1996	15,849	3,441	1,429
1997	16,120	3,552	1,616
1998	16,750	3,423	1,779
1999	16,010	3,608	1,983

a Includes hydrated limes.

Table 3-8: Hydrated Lime Production (Thousand Metric Tons)

Year	High-Calcium Hydrate	Dolomitic Hydrate
1990	1,777	323
1991	1,836	334
1992	1,887	343
1993	1,904	346
1994	1,938	352
1995	2,023	367
1996	1,853	337
1997	1,820	352
1998	1,950	383
1999	1,910	298

<sup>&</sup>lt;sup>b</sup> Includes dead-burned dolomite

alumina, and silica. Due to differences in the limestone used as a raw material, a rigid specification of lime material is impossible. As a result, few plants manufacture lime with exactly the same properties.

In addition, a portion of the CO<sub>2</sub> emitted during lime manufacture will actually be reabsorbed when the lime is consumed. As noted above, lime has many different chemical, industrial, environmental, and construction applications. In many processes, CO<sub>2</sub> reacts with the lime to create calcium carbonate (e.g., water softening). Carbon dioxide reabsorption rates vary, however, depending on the application. For example, 100 percent of the lime used to produce precipitated calcium carbonate (PCC) reacts with CO<sub>2</sub>; whereas most of the lime used in steelmaking reacts with impurities such as silica, sulfur, and aluminum compounds. A detailed accounting of lime use in the United States and further research into the associated processes are required to quantify the amount of CO<sub>2</sub> that is reabsorbed.<sup>5</sup> As more information becomes available, this emission estimate will be adjusted accordingly.

In some cases, lime is generated from calcium carbonate by-products at paper mills and water treatment plants. The lime generated by these processes is not included in the USGS data for commercial lime consumption. In the paper industry, mills that employ the sulfate process (i.e., Kraft) consume lime in order to causticize a waste sodium carbonate solution (i.e., black liquor). Most sulfate mills recover the waste calcium carbonate after the causticizing operation and calcine it back into lime—thereby generating CO<sub>2</sub>—for reuse in the pulping process. However, some of these mills capture the CO<sub>2</sub> released in this process to be used as precipitated calcium carbonate (PCC). Further research is necessary to determine to what extent CO<sub>2</sub> is released to the atmosphere through generation of lime by paper mills.

In the case of water treatment plants, lime is used in the softening process. Some large water treatment plants may recover their waste calcium carbonate and calcine it into quicklime for reuse in the softening process. Further research is necessary to determine the degree to which lime recycling is practiced by water treatment plants in the United States.

# **Limestone and Dolomite Use**

Limestone (CaCO<sub>3</sub>) and dolomite (CaCO<sub>3</sub>MgCO<sub>3</sub>)<sup>7</sup> are basic raw materials used by a wide variety of industries, including construction, agriculture, chemical, metallurgy, glass manufacture, and environmental pollution control. Limestone is widely distributed throughout the world in deposits of varying sizes and degrees of purity. Large deposits of limestone occur in nearly every State in the United States, and significant quantities are extracted for industrial applications. For some of these applications, limestone is sufficiently heated during the process to generate CO<sub>2</sub> as a by-product. Examples of such applications include limestone used as a flux or purifier in metallurgical furnaces, as a sorbent in flue gas desulfurization (FGD) systems for utility and industrial plants, or as a raw material in glass manufacturing.

In 1999, approximately 16,568 thousand metric tons of limestone and 2,068 thousand metric tons of dolomite were used for these applications. Overall, both limestone and dolomite usage resulted in aggregate  $CO_2$  emissions of 8.3 Tg  $CO_2$  Eq. (8,290 Gg) (see Table 3-9 and Table 3-10).

Emissions in 1999 increased 2 percent from the previous year and 62 percent since 1990. In the future, increases in demand for crushed stone are anticipated. Demand for crushed stone from the transportation sector continues to drive growth in limestone and dolomite use. The Transportation Equity Act for the 21st Century, which commits over \$200 billion dollars to highway work through 2003, is expected to maintain the upward trend in consumption.

 $<sup>^{5}</sup>$  Representatives of the National Lime Association estimate that  $CO_2$  reabsorption that occurs from the use of lime offsets as much as a third of the  $CO_2$  emissions from calcination.

<sup>&</sup>lt;sup>6</sup> Some carbide producers may also regenerate lime from their calcium hydroxide by-products, which does not result in emissions of  $CO_2$ . In making calcium carbide, quicklime is mixed with coke and heated in electric furnaces. The regeneration of lime in this process is done using a waste calcium hydroxide (hydrated lime)  $[CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2]$ , not calcium carbonate  $[CaCO_3]$ . Thus, the calcium hydroxide is heated in the kiln to simply expel the water  $[Ca(OH)_2 + heat \rightarrow CaO + H_2O]$  and no  $CO_2$  is released to the atmosphere.

<sup>&</sup>lt;sup>7</sup> Limestone and dolomite are collectively referred to as limestone by the industry, and intermediate varieties are seldom distinguished.

Table 3-9: CO<sub>2</sub> Emissions from Limestone & Dolomite Use (Tg CO<sub>2</sub> Eq.)

Activity	1990		1995	1996	1997	1998	1999	
Flux Stone	3.0		3.9	4.2	5.0	5.1	5.3	
Glass Making	0.2		0.5	0.4	0.4	0.2	0.2	
FGD	1.9		2.6	2.7	2.9	2.8	2.8	
Total 5.1 7.0 7.3 8.3 8.1 8.3								
Note: Totals may not	Note: Totals may not sum due to independent rounding.							

Table 3-10: CO<sub>2</sub> Emissions from Limestone & Dolomite Use (Gg)

Activity	1990	1995	1996	1997	1998	1999
Flux Stone	3,005	3,903	4,249	5,042	5,142	5,312
Limestone	2,554	2,523	3,330	3,970	4,298	4,441
Dolomite	452	1,380	919	1,072	844	871
Glass Making	189	526	362	383	191	197
Limestone	189	421	251	266	65	67
Dolomite	NA	105	110	117	125	129
FGD	1,922	2,558	2,695	2,902	2,781	2,781
Total	5,117	6,987	7,305	8,327	8,114	8,290

NA (Not Available)

Note: Totals may not sum due to independent rounding.

# Methodology

Carbon dioxide emissions were calculated by multiplying the amount of limestone consumed by an average carbon content for limestone, approximately 12.0 percent for limestone and 13.2 percent for dolomite (based on stoichiometry). Assuming that all of the carbon was oxidized and released to the atmosphere, the appropriate emission factor was multiplied by the annual level of consumption for flux stone, glass manufacturing, and FGD systems to determine emissions.

## **Data Sources**

Consumption data for 1990 through 1999 of limestone and dolomite used as flux stone and in glass manufacturing (see Table 3-11) were obtained from the USGS (1993, 1995a, 1995b, 1996, 1997, 1998, 1999, 2000). Consumption data for limestone used in FGD were taken from unpublished survey data in the Energy Information Administration's Form EIA-767, "Steam Electric Plant Operation and Design Report" (EIA 1997, 1998, 1999). For 1990 and 1994, the USGS did not provide a breakdown of limestone and dolomite production by end-use and for

**Table 3-11: Limestone and Dolomite Consumption (Thousand Metric Tons)** 

Activity	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999
Flux Stone	6,737	6,052	5,185	4,263	5,487	8,586	9,468	11,239	11,512	11,893
Limestone	5,804	5,213	4,447	3,631	3,149	5,734	7,569	9,024	9,769	10,093
Dolomite	933	838	738	632	2,339	2,852	1,899	2,215	1,743	1,801
Glass Making	430	386	495	622	949	1,174	799	847	407	421
Limestone	430	386	495	622	949	958	571	605	148	153
Dolomite	NA	NA	NA	NA	NA	216	228	242	259	267
FGD	4,369	4,606	4,479	4,274	5,080	5,815	6,125	6,595	6,322	6,322

NA (Not Available)

1999 the end-use breakdowns had not yet been finalized at the time of publication. Consumption figures for these years were estimated by assuming that limestone and dolomite accounted for the same percentage of total crushed stone consumption for a given year as the average of the percentages for the years before and after.<sup>8</sup> Furthermore, following 1996, limestone used in glass manufacture has only been reported for 1998. For 1996 and 1997, limestone used in glass manufacture was estimated based on the percent of total crushed stone for 1995 and 1998.

It should be noted that there is a large quantity of crushed stone reported to the USGS under the category "unspecified uses." A portion of this consumption is believed to be limestone or dolomite used as flux stone and for glass manufacture. The quantity listed for "unspecified uses" was therefore allocated to each reported enduse according to each end-use's fraction of total consumption in that year.<sup>9</sup>

# **Uncertainty**

Uncertainties in this estimate are due in part to variations in the chemical composition of limestone. In addition to calcite, limestone may contain smaller amounts of magnesia, silica, and sulfur. The exact specifications for limestone or dolomite used as flux stone vary with the pyrometallurgical process, the kind of ore processed, and the final use of the slag. Similarly, the quality of the limestone used for glass manufacturing will depend on the type of glass being manufactured.

Uncertainties also exist in the activity data. Much of the limestone consumed in the United States is reported as "other unspecified uses;" therefore, it is difficult to accurately allocate this unspecified quantity to the correct end-uses. Also, some of the limestone reported as "limestone" is believed to actually be dolomite, which has a higher carbon content than limestone. Lastly, the uncertainty of the estimates for limestone used in glass

making are especially high. Large fluctuations in reported consumption exist, reflecting year-to-year changes in the number of survey respondees. The uncertainty resulting from a shifting survey population is exacerbated by the gaps in the time series of reports. However, since glass making accounts for no more than 10 percent of limestone consumption, its contribution to the overall emissions estimate is low.

# **Soda Ash Manufacture** and Consumption

Soda ash (sodium carbonate, Na<sub>2</sub>CO<sub>3</sub>) is a white crystalline solid that is readily soluble in water and strongly alkaline. Commercial soda ash is used as a raw material in a variety of industrial processes and in many familiar consumer products such as glass, soap and detergents, paper, textiles, and food. It is used primarily as an alkali, either in glass manufacturing or simply as a material that reacts with and neutralizes acids or acidic substances. Internationally, two types of soda ash are produced—natural and synthetic. The United States produces only natural soda ash and is the largest soda ash-producing country in the world. Trona is the principal ore from which natural soda ash is made.

Only two States produce natural soda ash: Wyoming and California. Of these two States, only Wyoming has net emissions of CO<sub>2</sub>. This difference is a result of the production processes employed in each State. <sup>10</sup> During the production process used in Wyoming, natural sources of sodium carbonate are heated and transformed into a crude soda ash that requires further refining. Carbon dioxide (CO<sub>2</sub>) is generated as a by-product of this reaction, and is eventually emitted into the atmosphere. In addition, CO<sub>2</sub> may also be released when soda ash is consumed.

In 1999, CO<sub>2</sub> emissions from the manufacture of soda ash from trona were approximately 1.5 Tg CO<sub>2</sub> Eq.

<sup>&</sup>lt;sup>8</sup> Exception: 1990 and 1999 consumption were estimated using the percentages for only 1991 and 1998, respectively.

<sup>&</sup>lt;sup>9</sup> This approach was recommended by USGS.

 $<sup>^{10}</sup>$  In California, soda ash is manufactured using sodium carbonate-bearing brines instead of trona ore. To extract the sodium carbonate, the complex brines are first treated with  $\mathrm{CO}_2$  in carbonation towers to convert the sodium carbonate into sodium bicarbonate, which then precipitates from the brine solution. The precipitated sodium bicarbonate is then calcined back into sodium carbonate. Although  $\mathrm{CO}_2$  is generated as a by-product, the  $\mathrm{CO}_2$  is recovered and recycled for use in the carbonation stage and is not emitted.

Table 3-12: CO<sub>2</sub> Emissions from Soda Ash Manufacture and Consumption

Year	Tg CO <sub>2</sub> Eq.
1990	4.1
1996	4.3
1997	4.4
1998	4.3
1999	4.2

(1,549 Gg). Soda ash consumption in the United States also generated 2.7 Tg CO<sub>2</sub> Eq. (2,668 Gg) in 1999. Total emissions from this source in 1999 were then 4.2 Tg CO<sub>2</sub> Eq. (4,217 Gg) (see Table 3-12 and Table 3-13). Emissions have fluctuated since 1990. These fluctuations were strongly related to the behavior of the export market and the U.S. economy. Emissions in 1999 decreased by 3 percent from the previous year, but have increased 2 percent since 1990.

The United States has the world's largest deposits of trona and represents about one-third of total world soda ash output. The distribution of soda ash by enduse in 1999 was glass making, 51 percent; chemical production, 26 percent; soap and detergent manufacturing, 11 percent; distributors, 5 percent; flue gas desulfurization, pulp and paper production, and water treatment, 2 percent each; and miscellaneous constituted for the remaining 1 percent (USGS 2000).

Soda ash production and consumption decreased by 4 and 2 percent from 1998 values, respectively. Exports were a driving force behind U.S. soda ash production and the Asian economic crisis beginning in late 1997 has been cited as a major cause for the drop in world soda ash demand. However, growing demand in Asia and South America is expected to lead to moderate growth (between 0.5 and 1 percent) in U.S. soda ash production.

Construction is currently underway on a major soda ash plant that will use a new feedstock—nahcolite, a natural sodium bicarbonate found in deposits in Colorado's Piceance Creek Basin. The new facility will have an annual capacity of 900,000 tons of soda ash and is slated to

Table 3-13: CO<sub>2</sub> Emissions from Soda Ash Manufacture and Consumption (Gg)

Year	Manufacture	Consumption	Total
1990	1,435	2,709	4,144
1995	1,607	2,702	4,309
1996	1,587	2,685	4,273
1997	1,666	2,768	4,434
1998	1,607	2,718	4,325
1999	1,549	2,668	4,217
Note: Totals	may not sum due to	independent round	ing.

open in January 2001 (USGS 2000). Part of this production process involves the stripping of CO<sub>2</sub>. At this point, however, it is unknown whether any CO<sub>2</sub> will be released to the atmosphere or captured and used for conversion back to sodium bicarbonate.

## Methodology

During the production process, trona ore is calcined in a rotary kiln and chemically transformed into a crude soda ash that requires further processing. Carbon dioxide and water are generated as by-products of the calcination process. Carbon dioxide emissions from the calcination of trona can be estimated based on the following chemical reaction:

$$2(Na_3H(CO_3)_2 \times 2H_2O) \rightarrow 3Na_2CO_3 + 5H_2O + CO_2$$
[trona] [soda ash]

Based on this formula, approximately 10.27 metric tons of trona are required to generate one metric ton of CO<sub>2</sub>. Thus, the 15.9 million metric tons of trona mined in 1999 for soda ash production (USGS 2000) resulted in CO<sub>2</sub> emissions of approximately 1.5 Tg CO<sub>2</sub> Eq. (1,549 Gg).

Once manufactured, most soda ash is consumed in glass and chemical production, with minor amounts in soap and detergents, pulp and paper, flue gas desulfurization and water treatment. As soda ash is consumed for these purposes, additional CO2 is usually emitted. In these applications, it is assumed that one mole of carbon is released for every mole of soda ash used. Thus, approximately 0.113 metric tons of carbon (or 0.415 metric tons of CO<sub>2</sub>) are released for every metric ton of soda ash consumed.

## **Data Sources**

The activity data for trona production and soda ash consumption (see Table 3-14) were taken from USGS (1994, 1995, 1996, 1997, 1998, 1999, 2000). Soda ash manufacture and consumption data were collected by the USGS from voluntary surveys of the U.S. soda ash industry. All six of the soda ash manufacturing operations in the United States completed surveys to provide data to the USGS.

# **Uncertainty**

Emissions from soda ash manufacture are considered to be relatively certain. Both the emissions factor and activity data are reliable. However, emissions from soda ash consumption are dependent upon the type of processing employed by each end-use. Specific information characterizing the emissions from each end-use is limited. Therefore, uncertainty exists as to the accuracy of the emission factors.

# **Carbon Dioxide Consumption**

Carbon dioxide (CO<sub>2</sub>) is used for a variety of applications, including food processing, chemical production, carbonated beverages, and enhanced oil recovery (EOR). Carbon dioxide used for EOR is injected into the ground to increase reservoir pressure, and is therefore considered sequestered. <sup>11</sup> For the most part, however, CO<sub>2</sub> used

Table 3-14: Soda Ash Manufacture and Consumption (Thousand Metric Tons)

Year	Manufacture*	Consumption
1990	14,734	6,527
1991	14,674	6,278
1992	14,900	6,360
1993	14,500	6,350
1994	14,600	6,240
1995	16,500	6,510
1996	16,300	6,470
1997	17,100	6,670
1998	16,500	6,550
1999	15,900	6,430

in non-EOR applications will eventually be released to the atmosphere.

Carbon dioxide is produced from a small number of natural wells, as a by-product from the production of chemicals (e.g., ammonia), or separated from crude oil and natural gas. Depending on the raw materials that are used, the by-product CO<sub>2</sub> generated during these production processes may already be accounted for in the CO<sub>2</sub> emission estimates from fossil fuel consumption (either during combustion or from non-fuel uses). For example, ammonia is primarily manufactured using natural gas as a feedstock. Carbon dioxide emissions from this process are accounted for in the Energy chapter under Fossil Fuel Combustion and, therefore, are not included here.

In 1999,  $CO_2$  emissions from this source not accounted for elsewhere were 1.6 Tg  $CO_2$  Eq. (1,572 Gg) (see Table 3-15). This amount represents an increase of 11 percent from the previous year and is 97 percent higher than emissions in 1990.

## Methodology

Carbon dioxide emission estimates were based on  $\mathrm{CO}_2$  consumption with the assumption that the end-use applications, except enhanced oil recovery, eventually release 100 percent of the  $\mathrm{CO}_2$  into the atmosphere. Carbon dioxide consumption for uses other than enhanced oil re-

Table 3-15: CO<sub>2</sub> Emissions from Carbon Dioxide Consumption

800
968
1,140
1,294
1,413
1,572

<sup>\*</sup> Soda ash manufactured from trona ore only.

 $<sup>^{11}</sup>$  It is unclear to what extent the  $\mathrm{CO}_2$  used for EOR will be re-released. For example, the  $\mathrm{CO}_2$  used for EOR may show up at the wellhead after a few years of injection (Hangebrauk et al. 1992). This  $\mathrm{CO}_2$ , however, is typically recovered and re-injected into the well. More research is required to determine the amount of  $\mathrm{CO}_2$  that in fact escapes from EOR operations. For the purposes of this analysis, it is assumed that all of the  $\mathrm{CO}_2$  remains sequestered.

covery was about 7,861 thousand metric tons in 1999. The Freedonia Group estimates that, in the United States, there is an 80 to 20 percent split between  $CO_2$  produced as a byproduct and  $CO_2$  produced from natural wells. Thus, emissions are equal to 20 percent of  $CO_2$  consumption. The remaining 80 percent was assumed to already be accounted for in the  $CO_2$  emission estimates from other categories (the most important being Fossil Fuel Combustion).

## **Data Sources**

Carbon dioxide consumption data (see Table 3-16) were obtained from *Industrial Gases* to 2003, published by the Freedonia Group Inc. (1994, 1996, 1999a, 1999b). The 1999 report contains actual data for 1998 only. Data for 1996 were obtained by personal communication with Paul Ita of the Freedonia Group Inc. (Ita 1997). Data for 1997 and 1999 production were calculated from annualized growth rates for 1994 through 1996 and 1996 through 1998 respectively. The 1997 and 1999 values for enhanced oil recovery were set equal to the 1998 value. The percent of carbon dioxide produced from natural wells was obtained from Freedonia Group Inc. (1991).

# **Uncertainty**

Uncertainty exists in the assumed allocation of carbon dioxide produced from fossil fuel by-products (80 percent) and carbon dioxide produced from wells (20 per-

**Table 3-16: Carbon Dioxide Consumption** 

Year	Thousand Metric Tons		
1990	4,000		
1991	4,200		
1992	4,410		
1993	4,559		
1994	4,488		
1995	4,842		
1996	5,702		
1997	6,468		
1998	7,067		
1999	7,861		

cent). In addition, it is possible that  $\mathrm{CO}_2$  recovery exists in particular end-use sectors. Contact with several organizations did not provide any information regarding recovery. More research is required to determine the quantity, if any, that may be recovered.

# **Iron and Steel Production**

In addition to being an energy intensive process, the production of iron and steel also generates process-related emissions of CO<sub>2</sub>. Iron is produced by first reducing iron oxide (ore) with metallurgical coke in a blast furnace to produce pig iron (impure iron of about 4 to 4.5 percent carbon by weight). Carbon dioxide is produced as the coke used in this process is oxidized. Steel (less than 2 percent carbon by weight) is produced from pig iron in a variety of specialized steel furnaces. The majority of CO<sub>2</sub> emissions come from the production of iron, with smaller amounts evolving from the removal of carbon from pig iron to produce steel.

Emissions of  $\mathrm{CO}_2$  from iron and steel production in 1999 were 71.8 Tg  $\mathrm{CO}_2$  Eq. (71,840 Gg). Emissions fluctuated significantly from 1990 to 1999 due to changes in domestic economic conditions and changes in imports and exports. For the past several years, pig iron production has experienced a downward trend. Production in 1999 was 7 percent lower than 1998, and 12 percent below 1995 levels. Asian economic problems and the availability of low-priced imports continue to keep growth in check (USGS 2000).

CO<sub>2</sub> emissions from iron and steel production are not included in totals for the Industrial Processes chapter because they are accounted for with Fossil Fuel Combustion emissions from industrial coking coal in the Energy chapter. Emissions estimates are presented here for informational purposes only (see Table 3-17). Additional CO<sub>2</sub> emissions also occur from the use of limestone or dolomite flux during production; however, these emissions are accounted for under Limestone and Dolomite Use.

 $<sup>^{12}</sup>$  Although the  $\mathrm{CO}_2$  emissions from the use of industrial coking coal as a reducing agent should be included in the Industrial Processes chapter, information to distinguish individual non-energy uses of fossil fuels is unfortunately not available in DOE/EIA fuel statistics.

Table 3-17: CO<sub>2</sub> Emissions from Iron and Steel Production

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	87.6	87,600
1995	81.4	81,440
1996	79.0	79,040
1997	79.4	79,360
1998	77.1	77,120
1999	71.8	71,840

Carbon dioxide emissions were calculated by multiplying annual estimates of pig iron production by the ratio of  $\rm CO_2$  emitted per unit of iron produced (1.6 metric ton  $\rm CO_2$ /metric ton iron). The emission factor employed was applied to both pig iron production and integrated pig iron plus steel production; therefore, emissions were estimated using total U.S. pig iron production for all uses including making steel.

## **Data Sources**

The emission factor was taken from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997). Production data for 1990 through 1997 (see Table 3-18) were obtained from the U.S. Geological Survey's (USGS) *Minerals Yearbook: Volume I-Metals and Minerals* (USGS 1995, 1996, 1997, 1998, 1999); data for 1999 were obtained from USGS's *Mineral Commodity Summaries* (2000).

# **Uncertainty**

The emission factor employed was assumed to be applicable to both pig iron production and integrated pig iron plus steel production. This assumption was made because the uncertainty in the factor is greater than the additional emissions generated when steel is produced from pig iron. Using plant-specific emission factors could yield a more accurate estimate, but these factors were not available. The most accurate alternative would be to calculate emissions based on the amount of reducing agent used, rather than on the amount of iron or steel produced; however, these data were also not available.

**Table 3-18: Pig Iron Production** 

Year	Thousand Metric Tons
1990	54,750
1991	44,100
1992	47,400
1993	48,200
1994	49,400
1995	50,900
1996	49,400
1997	49,600
1998	48,200
1999	44,900

# **Ammonia Manufacture**

Emissions of carbon dioxide ( $CO_2$ ) occur during the production of ammonia. In the United States, roughly 98 percent of synthetic ammonia is produced by catalytic steam reforming of natural gas, and the remainder is produced using naphtha (a petroleum fraction) or the electrolysis of brine at chlorine plants (EPA 1997). The former two fossil fuel-based reactions produce carbon monoxide and hydrogen gas; however, the latter reaction does not lead to  $CO_2$  emissions. Carbon monoxide (CO) in the first two processes is transformed into  $CO_2$  in the presence of a catalyst (usually a metallic oxide). The hydrogen gas is diverted and combined with nitrogen gas to produce ammonia. The  $CO_2$ , included in a gas stream with other process impurities, is absorbed by a scrubber solution. In regenerating the scrubber solution,  $CO_2$  is released.

$$CH_4 + H_2O \rightarrow 4H_2 + CO_2$$

$$3H_2 + N_2 \rightarrow 2NH_3$$

Emissions of  $CO_2$  from ammonia production in 1999 were 25.8 Tg  $CO_2$  Eq. (25,799 Gg). Carbon dioxide emissions from this source are not included in totals for the Industrial Processes chapter because these emissions are accounted for with non-energy use of natural gas under Fossil Fuel Combustion in the Energy chapter. Emissions estimates are presented here for informational purposes only (see Table 3-19).

 $<sup>^{13}</sup>$  Although the  $\mathrm{CO}_2$  emissions from the use of natural gas as a feedstock should be included in the Industrial Processes chapter, information to distinguish individual non-energy uses of fossil fuels is unfortunately not available in DOE/EIA fuel statistics.

Emissions of  $CO_2$  were calculated by multiplying annual estimates of ammonia production by an emission factor (1.5 metric ton  $CO_2$ /metric ton ammonia). It was assumed that all ammonia was produced using catalytic steam reformation, although small amounts may have been produced using chlorine brines. The actual amount produced using this latter method is not known, but assumed to be small.

#### **Data Sources**

The emission factor was taken from the *Revised* 1996 IPCC Guidelines (IPCC/UNEP/OECD/IEA 1997). Ammonia production data (see Table 3-20) were obtained from the Census Bureau of the U.S. Department of Commerce (Census Bureau 1998, 2000) as reported in *Chemical and Engineering News*, "Facts & Figures for the Chemical Industry."

## **Uncertainty**

It is uncertain how accurately the emission factor used represents an average across all ammonia plants. By using natural gas consumption data for each ammonia plant, more accurate estimates could be calculated. However, these consumption data are often considered confidential and are difficult to acquire. All ammonia production in this analysis was assumed to be from the same process; however, actual emissions could differ because processes other than catalytic steam reformation may have been used.

Table 3-19: CO<sub>2</sub> Emissions from Ammonia Manufacture

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	23.1	23,138
1995	23.7	23,682
1996	24.4	24,390
1997	24.3	24,346
1998	25.1	25,141
1999	25.8	25,799

# **Ferroalloy Production**

Carbon dioxide is emitted from the production of several ferroalloys. Ferroalloys are composites of iron and other elements often including silicon, manganese, and chromium. When incorporated in alloy steels, ferroalloys are used to alter the material properties of the steel. Estimates from two types of ferrosilicon (50 and 75 percent silicon) and silicon metal (about 98 percent silicon) have been calculated. Emissions from the production of ferrochromium and ferromanganese are not included here because of the small number of manufacturers of these materials. As a result, government information disclosure rules prevent the publication of production data for them. Similar to emissions from the production of iron and steel, CO<sub>2</sub> is emitted when metallurgical coke is oxidized during a high-temperature reaction with iron and the selected alloying element. Due to the strong reducing environment, CO is initially produced. The CO is eventually oxidized, becoming CO<sub>2</sub>. A representative reaction equation for the production of 50 percent ferrosilicon is given below:

Emissions of  $\mathrm{CO}_2$  from ferroalloy production in 1999 were  $1.8\,\mathrm{Tg}\,\mathrm{CO}_2\,\mathrm{Eq}$ . (1,771 Gg). Carbon dioxide emissions from this source are not included in the totals for the Industrial Processes chapter because these emissions are accounted for in the calculations for industrial coking coal under Fossil Fuel Combustion in the Energy chapter. He Emission estimates are presented here for informational purposes only (see Table 3-21).

**Table 3-20: Ammonia Manufacture** 

Year	Thousand Metric Tons		
1990	15,425		
1991	15,576		
1992	16,261		
1993	15,599		
1994	16,211		
1995	15,788		
1996	16,260		
1997	16,231		
1998	16,761		
1999	17,200		

<sup>&</sup>lt;sup>14</sup> Although the CO<sub>2</sub> emissions from the use of industrial coking coal as a reducing agent should be included in the Industrial Processes chapter, information to distinguish individual non-energy uses of fossil fuels is unfortunately not available in DOE/EIA fuel statistics.

Emissions of CO<sub>2</sub> were calculated by multiplying annual ferroalloy production by material-specific emission factors. Emission factors were applied to production data for ferrosilicon 50 and 75 percent (2.35 and 3.9 metric ton CO<sub>2</sub>/metric ton, respectively) and silicon metal (4.3 metric ton CO<sub>2</sub>/metric ton). It was assumed that all ferroalloy production was produced using coking coal, although some ferroalloys may have been produced with wood, other biomass, or graphite carbon inputs.

## **Data Sources**

Emission factors were taken from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997). Ferroalloy production data for 1990 through 1998 (see Table 3-22) were obtained from the U.S. Geological Survey's (USGS) *Minerals Yearbook: Volume I—Metals and Minerals* (USGS, 1991, 1992, 1993, 1994, 1995, 1996, 1997, 1998, 1999, 2000); data for 1999 for ferrosilicon 75 percent and silicon metal were obtained from USGS (2000) *Mineral Industry Surveys: Silicon in December 1999*. Data for ferrosilicon 50 percent are no longer provided separately in USGS Mineral Industry Surveys, so the 1999 value was forecasted using the average annual growth in ferrosilicon 50 percent production for 1995 through 1998.

# **Uncertainty**

Although some ferroalloys may be produced using wood or other biomass as a carbon source, information and data regarding these practices were not available. Emissions from ferroalloys produced with wood would not be counted under this source because wood-based carbon is of biogenic origin. Emissions from ferroalloys produced with graphite inputs would be counted in national totals, but may generate differing amounts of CO<sub>2</sub> per unit of ferroalloy produced compared to the use of coking coal. As with emissions from iron and steel production, the most accurate method for these estimates would be basing calculations on the amount of reducing agent used in the process, rather than on the amount of ferroalloys produced. These data were not available, however.

Table 3-21: CO<sub>2</sub> Emissions from Ferroalloy Production

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	1.8	1,809
1995	1.6	1,625
1996	1.7	1,695
1997	1.8	1,789
1998	1.8	1,793
1999	1.8	1,771

# **Petrochemical Production**

Small amounts of methane ( $\mathrm{CH_4}$ ) are released during the production of some petrochemicals. Petrochemicals are chemicals isolated or derived from petroleum or natural gas. Emissions are presented here from the production of five chemicals: carbon black, ethylene, ethylene dichloride, styrene, and methanol.

Carbon black is an intensely black powder made by the incomplete combustion of an aromatic petroleum feedstock. Almost all output is added to rubber to impart strength and abrasion resistance, and the tire industry is by far the largest consumer. Ethylene is consumed in the production processes of the plastics industry including

**Table 3-22: Production of Ferroalloys (Metric Tons)** 

Year	Ferrosilicon 50%	Ferrosilicon 75%	Silicon Metal
1990	321,385	109,566	145,744
1991	230,019	101,549	149,570
1992	238,562	79,976	164,326
1993	199,275	94,437	158,000
1994	198,000	112,000	164,000
1995	181,000	128,000	163,000
1996	182,000	132,000	175,000
1997	175,000	147,000	187,000
1998	162,000	147,000	195,000
1999	156,121	145,000	195,000

<sup>&</sup>lt;sup>15</sup> Emissions and sinks of biogenic carbon are accounted for in the Land-Use Change and Forestry chapter.

polymers such as high, low, and linear low density polyethylene (HDPE, LDPE, LLDPE), polyvinyl chloride (PVC), ethylene dichloride, ethylene oxide, and ethylbenzene. Ethylene dichloride is one of the first manufactured chlorinated hydrocarbons with reported production as early as 1795. In addition to being an important intermediate in the synthesis of chlorinated hydrocarbons, ethylene dichloride is used as an industrial solvent and as a fuel additive. Styrene is a common precursor for many plastics, rubber, and resins. It can be found in many construction products, such as foam insulation, vinyl flooring, and epoxy adhesives. Methanol is an alternative transportation fuel as well as a principle ingredient in windshield wiper fluid, paints, solvents, refrigerants, and disinfectants. In addition, methanol-based acetic acid is used in making PET plastics and polyester fibers. The United States produces close to one quarter of the world's supply of methanol.

Aggregate emissions of  $\mathrm{CH_4}$  from petrochemical production in 1999 were 1.7  $\mathrm{Tg}\,\mathrm{CO_2}\,\mathrm{Eq.}$  (79  $\mathrm{Gg}\,\mathrm{CH_4}$ ) (see Table 3-23). Production levels of all five chemicals have shown steady growth over the past 5 years, with increases ranging from 2 to 4 percent. However, petrochemicals are currently in oversupply and production for 2000 is expected to decrease slightly.

Table 3-23: CH<sub>4</sub> Emissions from Petrochemical Production

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	1.2	56
1995	1.5	72
1996	1.6	75
1997	1.6	77
1998	1.6	77
1999	1.7	79

## Methodology

Emissions of CH<sub>4</sub> were calculated by multiplying annual estimates of chemical production by an emission factor. The following factors were used: 11 kg CH<sub>4</sub>/metric ton carbon black, 1 kg CH<sub>4</sub>/metric ton ethylene, 0.4 kg CH<sub>4</sub>/metric ton ethylene dichloride, <sup>16</sup> 4 kg CH<sub>4</sub>/metric ton styrene, and 2 kg CH<sub>4</sub>/metric ton methanol. These emission factors were based upon measured material balances. Although the production of other chemicals may also result in methane emissions, there were not sufficient data to estimate their emissions.

## **Data Sources**

Emission factors were taken from the Revised 1996 IPCC Guidelines (IPCC/UNEP/OECD/IEA 1997). Annual production data for 1990 through 1998 (see Table 3-24) were obtained from the *Chemical Manufacturer's Association Statistical Handbook* (CMA 1999). Production for 1999 was projected using each chemical's average annual growth rate for 1993 through 1998.

**Table 3-24: Production of Selected Petrochemicals (Thousand Metric Tons)** 

Chemical	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999
Carbon Black	1,306	1,225	1,365	1,452	1,492	1,524	1,560	1,588	1,610	1,644
Ethylene	16,542	18,124	18,563	18,709	20,201	21,199	22,197	23,088	23,474	24,563
Ethylene Dichloride	6,282	6,221	6,872	8,141	8,482	7,829	8,596	9,152	8,868	9,021
Styrene	3,637	3,681	4,082	4,565	5,112	5,167	5,387	5,171	5,183	5,316
Methanol	3,785	3,948	3,666	4,782	4,904	4,888	5,330	5,806	5,693	5,895

<sup>&</sup>lt;sup>16</sup> The emission factor obtained from IPCC/UNEP/OECD/IEA (1997), page 2.23 is assumed to have a misprint; the chemical identified should be dichloroethylene ( $C_2H_2Cl_2$ ) instead of ethylene dichloride ( $C_2H_4Cl_2$ ).

## **Uncertainty**

The emission factors used here were based on a limited number of studies. Using plant-specific factors instead of average factors could increase the accuracy of the emissions estimates, however, such data were not available. There may also be other significant sources of methane arising from petrochemical production activities that have not been included in these estimates.

# **Silicon Carbide Production**

Methane is emitted from the production of silicon carbide, a material used as an industrial abrasive. To make silicon carbide (SiC), quartz (SiO<sub>2</sub>) is reacted with carbon in the form of petroleum coke. Methane is produced during this reaction from volatile compounds in the petroleum coke. Although  $\rm CO_2$  is also emitted from this production process, the requisite data were unavailable for these calculations. Regardless, they are already accounted for under  $\rm CO_2$  from Fossil Fuel Combustion in the Energy chapter. Emissions of  $\rm CH_4$  from silicon carbide production in 1999 (see Table 3-25) were 1 Gg  $\rm CH_4$  (less than 0.05 Tg  $\rm CO_2$  Eq.).

# Methodology

Emissions of  $\mathrm{CH_4}$  were calculated by multiplying annual silicon carbide production by an emission factor (11.6 kg  $\mathrm{CH_4/metric}$  ton silicon carbide). This emission factor was derived empirically from measurements taken at Norwegian silicon carbide plants (IPCC/UNEP/OECD/IEA 1997).

Table 3-25: CH<sub>4</sub> Emissions from Silicon Carbide Production

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	+	1
1995	+	1
1996	+	1
1997	+	1
1998	+	1
1999	+	1
+ Does not exceed 0.0	5 Tg CO <sub>2</sub> Eq.	

#### **Data Sources**

The emission factor was taken from the *Revised* 1996 IPCC Guidelines (IPCC/UNEP/OECD/IEA 1997). Production data for 1990 through 1998 (see Table 3-26) were obtained from the *Minerals Yearbook: Volume I-Metals and Minerals, Manufactured Abrasives* (USGS 1991, 1992, 1993, 1994, 1995, 1996, 1997, 1998, 1999, 2000).

## **Uncertainty**

The emission factor used here was based on one study of Norwegian plants. The applicability of this factor to average U.S. practices at silicon carbide plants is uncertain. A better alternative would be to calculate emissions based on the quantity of petroleum coke used during the production process rather than on the amount of silicon carbide produced. These data were not available, however.

# **Adipic Acid Production**

Adipic acid production has been identified as an anthropogenic source of nitrous oxide ( $N_2O$ ) emissions. Worldwide, there are few adipic acid plants. The United States is the major producer with three companies in four locations accounting for approximately forty percent of world production. Adipic acid is a white crystalline solid used in the manufacture of synthetic fibers, coatings, plastics, urethane foams, elastomers, and synthetic lubricants. Commercially, it is the most important of the aliphatic dicarboxylic acids, which are used to manufacture

**Table 3-26: Production of Silicon Carbide** 

Year	Metric Tons
1990	105,000
1991	78,900
1992	84,300
1993	74,900
1994	84,700
1995	75,400
1996	73,600
1997	68,200
1998	69,800
1999	69,800

polyesters. Approximately 80 percent of all adipic acid produced in the United States is used in the production of nylon 6,6. It is also used to provide some foods with a "tangy" flavor.

Adipic acid is produced through a two-stage process during which N<sub>2</sub>O is generated in the second stage. The first stage of manufacturing usually involves the oxidation of cyclohexane to form a cyclohexanone/ cyclohexanol mixture. The second stage involves oxidizing this mixture with nitric acid to produce adipic acid. Nitrous oxide is generated as a by-product of the nitric acid oxidation stage and is emitted in the waste gas stream. Process emissions from the production of adipic acid will vary with the types of technologies and level of emissions controls employed by a facility. In 1990, two of the three major adipic acid producing plants implemented N<sub>2</sub>O abatement technologies and as of 1998, all of the major adipic acid production facilities had control systems in place.<sup>17</sup> Only one small plant does not control for N<sub>2</sub>O, representing approximately 2 percent of production.

Adipic acid production for 1999 was 1,100 thousand metric tons. Nitrous oxide emissions from this source were estimated to be 9.0 Tg  $\rm CO_2$  Eq. (29 Gg) in 1999 (see Table 3-27).

In 1999, adipic acid production reached its highest level in fifteen years. This increase is chiefly due to a 120,000 metric ton expansion in production capacity and to rising demand for engineering plastics. Though production continues to increase, emissions have been significantly reduced due to the widespread installation of

Table 3-27: N<sub>2</sub>O Emissions from Adipic Acid Production

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	18.3	59
1995	20.3	66
1996	20.8	67
1997	17.1	55
1998	7.3	23
1999	9.0	29

pollution control measures. The  $N_2O$  abatement technology voluntarily implemented at the three major producing plants accounts for an overall reduction of emissions by approximately 51 percent between 1990 and 1999.

# Methodology

Nitrous oxide emissions were calculated by multiplying adipic acid production by the ratio of  $N_2O$  emitted per unit of adipic acid produced and adjusting for the actual percentage of  $N_2O$  released as a result of plant-specific emission controls. Because emissions of  $N_2O$  in the United States are not regulated, emissions have not been well characterized. However, on the basis of experiments (Thiemens and Trogler 1991), the overall reaction stoichiometry for  $N_2O$  production in the preparation of adipic acid was estimated at approximately  $0.3~{\rm kg}$  of  $N_2O$  per kilogram of product. Emissions are determined using the following equation:

 $N_2O$  emissions = [production of adipic acid] × [0.3 kg  $N_2O$  / kg adipic acid] × [1-( $N_2O$  destruction factor × abatement system utility factor)]

The " $N_2O$  destruction factor" represents the amount of  $N_2O$  expressed as a percentage of  $N_2O$  emissions that are destroyed by the currently installed abatement technology. The "abatement system utility factor" represents the percent of time that the abatement equipment operates. Overall, in the United States, 63 percent of production employs catalytic destruction, 34 percent uses thermal destruction, and 3 percent of production has no  $N_2O$  abatement measures. The  $N_2O$  abatement system destruction factor is assumed to be 95 percent for catalytic abatement and 98 percent for thermal abatement (Reimer et al. 1999, Reimer 1999). The abatement system utility factor is assumed to be 95 percent for catalytic abatement and 98 percent for thermal abatement (Reimer et al. 1999, Reimer 1999).

<sup>&</sup>lt;sup>17</sup> During 1997, the N<sub>2</sub>O emission controls installed by the third plant operated for approximately a quarter of the year.

## **Data Sources**

Adipic acid production data for 1990 through 1995 (see Table 3-28) were obtained from *Chemical and Engineering News*, "Facts and Figures" and "Production of Top 50 Chemicals" (C&EN 1992, 1993, 1994, 1995, 1996). For 1996 and 1997 data were projected from the 1995 manufactured total based upon suggestions from industry contacts. For 1998, production data were obtained from *Chemical Week*, Product focus: adipic acid/adiponitrile (CW 1999). Production data for 1999 are based on an estimate provided by the adipic acid industry (Reimer 2000). The emission factor was taken from Thiemens and Trogler (1991). Adipic acid plant capacities for 1998 and 1999 were updated using *Chemical Week*, Product focus: adipic acid/adiponitrile (CW 1999). Plant capacities for previous years were obtained from Chemical Market Reporter (1998).

## **Uncertainty**

Because  $N_2O$  emissions are controlled in some adipic acid production facilities, the amount of  $N_2O$  that is actually released will depend on the level of controls in place at a specific production plant. Thus, in order to calculate accurate emission estimates, it is necessary to have production data on a plant-specific basis. In most cases, however, these data are confidential. As a result, plant-specific production figures were estimated by allocating total adipic acid production using existing plant capacities. This creates a degree of uncertainty in the adipic acid production data used to derive the emission estimates as it is necessary to assume that all plants operate at equivalent utilization levels.

**Table 3-28: Adipic Acid Production** 

Year	Thousand Metric Tons
1990	735
1991	771
1992	708
1993	765
1994	815
1995	816
1996	835
1997	860
1998	866
1999	1,100

The emission factor was based on experiments (Thiemens and Trogler 1991) that attempt to replicate the industrial process and, thereby, measure the reaction stoichiometry for  $N_2O$  production in the preparation of adipic acid. However, the extent to which the lab results are representative of actual industrial emission rates is not known.

# **Nitric Acid Production**

Nitric acid (HNO<sub>3</sub>) is an inorganic compound used primarily to make synthetic commercial fertilizers. It is also a major component in the production of adipic acid—a feedstock for nylon—and explosives. Virtually all of the nitric acid produced in the United States is manufactured by the catalytic oxidation of ammonia (EPA 1997). During this reaction,  $N_2O$  is formed as a by-product and is released from reactor vents into the atmosphere.

Currently, the nitric acid industry controls for NO and  $NO_2$ , (i.e.,  $NO_x$ ). As such the industry uses a combination of non-selective catalytic reduction (NSCR) and selective catalytic reduction (SCR) technologies. In the process of destroying  $NO_x$ , NSCR systems are also very affective at destroying  $N_2O$ . However, NSCR units are generally not preferred in modern plants because of high energy costs and associated high gas temperatures. NSCRs were widely installed in nitric plants built between 1971 and 1977. Currently, it is estimated that approximately 20 percent of nitric acid plants use NSCR (Choe, et al. 1993). The remaining 80 percent use SCR or extended absorption, neither of which is known to reduce  $N_2O$ .

Nitric acid production was 8,165 thousand metric tons in 1999 (C&EN 2000). Nitrous oxide emissions from this source were estimated at  $20.2 \text{ Tg CO}_2 \text{ Eq.}$  (65 Gg) (see Table 3-29). Emissions from nitric acid production decreased slightly in 1999, but have increased 13 percent since 1990.

# Methodology

Nitrous oxide emissions were calculated by multiplying nitric acid production by the amount of  $N_2O$  emitted per unit of nitric acid produced. The emissions factor was determined as a weighted average of 2 kg for plants using non-selective catalytic reduction (NSCR) systems and 9.5

Table 3-29: N<sub>2</sub>0 Emissions from Nitric Acid Production

Year	Tg CO <sub>2</sub> Eq.	Gg	
1990	17.8	58	
1995	19.9	64	
1996	20.7	67	
1997	21.2	68	
1998	20.9	67	
1999	20.2	65	

kg for plants not equipped with NSCR (Reimer et al. 1992). An estimated 20 percent of HNO<sub>3</sub> plants in the U.S. were equipped with NSCR (Choe, et al. 1993). In the process of destroying NO<sub>x</sub>, NSCR systems also destroy 80 to 90 percent of the N<sub>2</sub>O. Hence, the emission factor is equal to (9.5  $\times$  0.80) + (2  $\times$  0.20) = 8 kg N<sub>2</sub>O / metric ton HNO<sub>3</sub>.

### **Data Sources**

Nitric acid production data for 1990 through 1999 (see Table 3-30) were obtained from *Chemical and Engineering News*, "Facts and Figures" (C&EN 2000). The emission factor range was taken from Reimer et al. (1992).

# **Uncertainty**

In general, the nitric acid industry is not well categorized. A significant degree of uncertainty exists in nitric acid production figures because nitric acid plants are often part of larger production facilities, such as fertilizer or explosive manufacturing. As a result, only a small volume of nitric acid is sold on the market making production quantities difficult to track. Emission factors are also difficult to determine because of the large number of plants using many different technologies. Based on expert judgment, it is estimated that the  $N_2\mathrm{O}$  destruction factor for NSCR nitric acid facilities is associated with an uncertainty of approximately  $\pm$  10 percent.

**Table 3-30: Nitric Acid Production** 

Year	Thousand Metric Tons
1990	7,196
1991	7,191
1992	7,381
1993	7,488
1994	7,905
1995	8,020
1996	8,351
1997	8,557
1998	8,423
1999	8,165

# **Substitution of Ozone Depleting Substances**

Hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs) are used primarily as alternatives to several classes of ozone-depleting substances (ODSs) that are being phased out under the terms of the Montreal Protocol and the Clean Air Act Amendments of 1990. 18 Ozone depleting substances—chlorofluorocarbons (CFCs), halons, carbon tetrachloride, methyl chloroform, and hydrochlorofluorocarbons (HCFCs)—are used in a variety of industrial applications including refrigeration and air conditioning equipment, solvent cleaning, foam production, sterilization, fire extinguishing, and aerosols. Although HFCs and PFCs, unlike ODSs, are not harmful to the stratospheric ozone layer, they are potent greenhouse gases. Emission estimates for HFCs and PFCs used as substitutes for ODSs are provided in Table 3-31 and Table 3-32.

In 1990 and 1991, the only significant emissions of HFCs and PFCs as substitutes to ODSs were relatively small amounts of HFC-152a—a component of the refrigerant blend R-500 used in chillers—and HFC-134a in refrigeration end-uses. Beginning in 1992, HFC-134a was used in growing amounts as a refrigerant in motor vehicle air conditioners and in refrigerant blends such as R-404. In 1993, use of HFCs in foams and aerosols began, and in

<sup>&</sup>lt;sup>18</sup> [42 U.S.C § 7671, CAA § 601]

<sup>&</sup>lt;sup>19</sup> R-404 contains HFC-125, HFC-143a, and HFC-134a.

Table 3-31: Emissions of HFCs and PFCs from ODS Substitution (Tg CO<sub>2</sub> Eq.)

Gas	1990	1995	1996	1997	1998	1999	
HFC-23	+	+	0.1	0.1	0.2	0.3	
HFC-32	+	+	+	+	+	+	
HFC-125	+	1.3	1.9	2.5	3.1	3.6	
HFC-134a	0.7	18.6	24.7	30.5	34.9	39.4	
HFC-143a	+	0.4	8.0	1.3	1.9	2.6	
HFC-236fa	+	+	+	0.1	0.8	1.3	
CF <sub>4</sub>	+	+	+	+	+	+	
Others*	0.2	3.6	6.6	7.6	8.8	9.4	
Total	0.9	24.0	34.0	42.1	49.6	56.7	

<sup>+</sup> Does not exceed 0.05 Tg CO<sub>2</sub> Eq.

Note: Totals may not sum due to independent rounding.

1994 these compounds also found applications as solvents and sterilants. In 1995, ODS substitutes for halons entered widespread use in the United States as halon production was phased-out.

The use and subsequent emissions of HFCs and PFCs as ODS substitutes has been increasing from small amounts in 1990 to 56.7 Tg CO<sub>2</sub> Eq. in 1999. This increase was the result of efforts to phase-out CFCs and other ODSs in the United States. In the short term, this trend is expected to continue, and will likely accelerate in the next decade as HCFCs, which are interim substitutes in many applications, are themselves phased out under the provisions of the Copenhagen Amendments to the *Montreal Protocol*. Improvements in the technologies associated with the use of these gases, however, may help to offset this anticipated increase in emissions.

# **Methodology and Data Sources**

The EPA used a detailed vintaging model of ODS-containing equipment and products to estimate the actual—versus potential—emissions of various ODS substitutes, including HFCs and PFCs. The name of the model refers to the fact that the model tracks the use and emissions of various compounds for the annual "vintages" of new equipment that enter service in each end-use. This

vintaging model predicts ODS and ODS substitute use in the United States based on modeled estimates of the quantity of equipment or products sold each year containing these chemicals and the amount of the chemical required to manufacture and/or maintain equipment and products over time. Emissions for each end-use were estimated by applying annual leak rates and release profiles, which account for the lag in emissions from equipment as they leak over time. By aggregating the data for more than 40 different end-uses, the model produces estimates of annual use and emissions of each compound. Details on the Vintaging Model are contained in Annex I.

# **Uncertainty**

Given that emissions of ODS substitutes occur from thousands of different kinds of equipment and from millions of point and mobile sources throughout the United States, emission estimates must be made using analytical tools such as the EPA vintaging model or the methods outlined in IPCC/UNEP/OECD/IEA (1997). Though the EPA's model is more comprehensive than the IPCC methodology, significant uncertainties still exist with regard to the levels of equipment sales, equipment characteristics, and end-use emissions profiles that were used to estimate annual emissions for the various compounds.

<sup>\*</sup> Others include HFC-152a, HFC-227ea, HFC-4310mee, and PFC/PFPEs, the latter being a proxy for a diverse collection of PFCs and perfluoropolyethers (PFPEs) employed for solvent applications. For estimating purposes, the GWP value used for PFC/PFPEs was based upon  $C_{6}F_{14}$ .

Table 3-32: Emissions of HFCs and PFCs from ODS Substitution (Mg)

Gas	1990	1995	1996	1997	1998	1999
HFC-23	+	2	5	10	17	25
HFC-32	+	+	3	7	11	17
HFC-125	+	478	675	889	1,116	1,289
HFC-134a	564	14,345	18,962	23,478	26,854	30,340
HFC-143a	+	111	209	334	488	676
HFC-236fa	+	+	+	15	120	213
CF <sub>4</sub>	+	+	+	+	+	1
Others*	M	M	M	M	M	M

M (Mixture of Gases)

# **Aluminum Production**

Aluminum is a light-weight, malleable, and corrosion resistant metal that is used in many manufactured products including aircraft, automobiles, bicycles, and kitchen utensils. In 1999, the United States was the largest producer of primary aluminum, with 16 percent of the world total (USGS 2000). The United States was also a major importer of primary aluminum. The production of primary aluminum—in addition to consuming large quantities of electricity—results in process-related emissions of several greenhouse gases including carbon dioxide  $(CO_2)$  and two perfluorocarbons (PFCs): perfluoromethane  $(CF_4)$  and perfluoroethane  $(C_7F_6)$ .

Occasionally, sulfur hexafluoride ( $SF_6$ ) is also used by the aluminum industry as a cover gas or a fluxing and degassing agent in experimental and specialized casting operations. In its application as a cover gas,  $SF_6$  is mixed with nitrogen or carbon dioxide and injected above the surface of molten aluminum; as a fluxing and degassing agent,  $SF_6$  is mixed with argon, nitrogen, and/or chlorine and blown through molten aluminum. These practices are not employed extensively by primary aluminum producers and are probably isolated to the secondary casting firms. The aluminum industry in the United States and Canada is estimated to use 230 Mg of  $SF_6$  per year (Maiss and Brenninkmeijer 1998); however, this estimate is highly uncertain.

Historically,  $SF_6$  from aluminum activities has been omitted from models of global  $SF_6$  emissions, with the

caveat that any emissions would be insignificant (Ko et al. 1993, Victor and MacDonald 1998). Emissions are thought to be slight since the concentration of  $SF_6$  in the mixtures is small and a portion of the  $SF_6$  is decomposed in the process (MacNeal et al. 1990, Gariepy and Dube 1992, Ko et al. 1993, Ten Eyck and Lukens 1996, Zurecki 1996). Emissions of  $SF_6$  have not been estimated for aluminum production.

Carbon dioxide is emitted during the aluminum smelting process when alumina (aluminum oxide, Al<sub>2</sub>O<sub>3</sub>) is reduced to aluminum using the Hall-Heroult reduction process. The reduction of the alumina occurs through electrolysis in a molten bath of natural or synthetic cryolite (Na<sub>3</sub>AlF<sub>6</sub>). The reduction cells contain a carbon lining that serves as the cathode. Carbon is also contained in the anode, which can be a carbon mass of paste, coke briquettes, or prebaked carbon blocks from petroleum coke. During reduction, some of this carbon is oxidized and released to the atmosphere as CO<sub>2</sub>.

Process emissions of CO<sub>2</sub> from aluminum production were estimated at 5.6 Tg CO<sub>2</sub> Eq. (5,555 Gg) in 1999 (see Table 3-33). The CO<sub>2</sub> emissions from this source, however, are accounted for under the non-energy use portion of CO<sub>2</sub> from Fossil Fuel Combustion of petroleum coke and tar pitch in the Energy chapter. Thus, to avoid double counting, CO<sub>2</sub> emissions from aluminum production are not included in totals for the Industrial Processes chapter. They are provided here for informational purposes only.

<sup>+</sup> Does not exceed 0.5 Mg

<sup>\*</sup> Others include HFC-152a, HFC-227ea, HFC-4310mee and PFC/PFPEs, which are a proxy for a diverse collection of PFCs and perfluoropolyethers (PFPEs) employed for solvent applications.

In addition to  $\mathrm{CO}_2$  emissions, the aluminum production industry is also the largest source of PFC emissions in the United States. During the smelting process, when the alumina ore content of the electrolytic bath falls below critical levels required for electrolysis, rapid voltage increases occur, termed "anode effects." These anode effects cause carbon from the anode and fluorine from the dissociated molten cryolite bath to combine, thereby producing fugitive emissions of  $\mathrm{CF}_4$  and  $\mathrm{C}_2\mathrm{F}_6$ . In general, the magnitude of emissions for a given level of production depends on the frequency and duration of these anode effects. The more frequent and long-lasting the anode effects, the greater the emissions.

Primary aluminum production-related emissions of PFCs are estimated to have declined 48 percent since 1990. Since 1990, emissions of  $CF_4$  and  $C_2F_6$  have declined 46 and 58 percent, respectively, to 9.0 Tg  $CO_2$  Eq. of  $CF_4$  (1.38 Gg  $CF_4$ ) and 1.1 Tg  $CO_2$  Eq. of  $C_2F_6$  (0.12 Gg  $C_2F_6$ ) in 1999, as shown in Table 3-34 and Table 3-35. This decline was both due to reductions in domestic aluminum production and actions taken by aluminum smelting companies to reduce the frequency and duration of anode effects. The EPA supports aluminum smelters with these efforts through the Voluntary Aluminum Industrial Partnership (VAIP).

U.S. primary aluminum production for 1999—totaling 3,779 thousand metric tons—increased slightly from 1998. This increase is attributed to the reintroduction of previously idled production capacity and the start up of new production capacity (USGS 2000). The transportation industry remained the largest domestic consumer of aluminum, accounting for about 37 percent (USGS 2000).

Table 3-33: CO<sub>2</sub> Emissions from Aluminum Production

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	6.0	5,951
1995	5.0	4,961
1996	5.3	5,258
1997	5.3	5,296
1998	5.5	5,458
1999	5.6	5,555

According to the U.S. Geological Survey (2000), overall consumption in the United States will continue to grow, driven by strong demand for aluminum in manufacturing passenger cars and light trucks. However, annual domestic production is expected to decline in 2000. The high cost of electric power in various regions of the country has prompted several production curtailments at U.S. smelters.

# Methodology

Carbon dioxide is generated during alumina reduction to aluminum metal following the reaction below:

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$$

The  $\mathrm{CO}_2$  emission factor employed was estimated from the production of primary aluminum metal and the carbon consumed by the process. During alumina reduction, approximately 1.5 to 2.2 metric tons of  $\mathrm{CO}_2$  are emitted for each metric ton of aluminum produced (Abrahamson 1992). Based upon the mass balance for a

Table 3-34: PFC Emissions from Aluminum Production (Tg CO<sub>2</sub> Eq.)

Year	CF <sub>4</sub>	$C_2F_6$	Total	
1990	16.7	2.5	19.3	
1995	10.0	1.3	11.2	
1996	10.3	1.3	11.6	
1997	9.7	1.2	10.8	
1998	9.0	1.1	10.1	
1999	9.0	1.1	10.0	

Note: Totals may not sum due to independent rounding.

Table 3-35: PFC Emissions from Aluminum Production (Gg)

Year	CF <sub>4</sub>	C <sub>2</sub> F <sub>6</sub>
1990	2.6	0.3
1995	1.5	0.1
1996	1.6	0.1
1997	1.5	0.1
1998	1.4	0.1
1999	1.4	0.1

"typical" aluminum smelter (Drexel University Project Team 1996), the emission factor was set at 1.5 metric tons  $CO_2$  per metric ton of aluminum smelted. This value is at the low end of the Abrahamson (1992) range.

The CO<sub>2</sub> emissions from this source are already accounted for under CO<sub>2</sub> Emissions from Fossil Fuel Combustion in the Energy chapter.<sup>20</sup> Thus, to avoid double counting, CO<sub>2</sub> emissions from aluminum production are not included in totals for the Industrial Processes chapter.

PFC emissions from aluminum production were estimated using a per unit production emission factor that is expressed as a function of operating parameters (anode effect frequency and duration), as follows:

PFC (CF<sub>4</sub> or C<sub>2</sub>F<sub>6</sub>) kg/metric ton Al =  $S \times Anode$ Effect Minutes/Cell-Day

where.

S = Slope coefficient

Anode Effect Minutes/Cell-Day = Anode Effect Frequency × Anode Effect Duration

The slope coefficient was established for each smelter based on actual field measurements, where available, or default coefficients by technology-type based on field measurements. Once established, the slope coefficient was used along with smelter anode effect data, collected by aluminum companies and reported to the VAIP, to estimate emissions factors over time. Emissions factors were multiplied by annual production to estimate annual emissions at the smelter level. Emissions were then aggregated across smelters to estimate national emissions. The methodology used to estimate emissions is consistent with the methodologies recommended by the *Good Practice Guidance* (IPCC 2000).

### **Data Sources**

Primary aluminum production data for 1990 through 1999 (see Table 3-36) were obtained from USGS, *Mineral Industry Surveys: Aluminum Annual Report* (USGS 1995, 1998, 2000). The USGS requested data from the 12 domestic producers, all of whom responded. The CO<sub>2</sub> emission factor range was taken from Abrahamson (1992). The mass

**Table 3-36: Production of Primary Aluminum** 

Year	Thousand Metric Tons
1990	4,048
1991	4,121
1992	4,042
1993	3,695
1994	3,299
1995	3,375
1996	3,577
1997	3,603
1998	3,713
1999	3,779

balance for a "typical" aluminum smelter was taken from Drexel University Project Team (1996).

PFC emission estimates were provided by the EPA in cooperation with participants in the Voluntary Aluminum Industrial Partnership (VAIP) program.

# **Uncertainty**

There is uncertainty as to the most accurate CO<sub>2</sub> emission factor for aluminum production. Emissions vary depending on the specific technology used by each plant. However, evidence suggests that there is little variation in CO<sub>2</sub> emissions from plants utilizing similar technologies (IPCC/UNEP/OECD/IEA 1997). A more accurate method would be to calculate emissions based upon the amount of carbon—in the form of petroleum coke or tar pitch—consumed by the process; however, this type of information was not available.

For PFC emission estimates, the uncertainty in the aluminum production data is relatively low ( $\pm$  1 to 2 percent) compared to the uncertainty in the emissions factors ( $\pm$  10 to 50 percent). Uncertainty in the emissions factors arises from the lack of comprehensive data for both the slope coefficients and anode effect data. Currently, insufficient measurement data exist to quantify a relationship between PFC emissions and anode effect minutes for all smelters. Future inventories will incorporate additional data reported by aluminum companies and ongoing research into PFC emissions from aluminum production.

 $<sup>^{20}</sup>$  Although the carbon contained in the anode is considered a non-energy use of petroleum coke or tar pitch and the  $\mathrm{CO}_2$  emissions it generates should be included in the Industrial Processes chapter, information needed to distinguish individual non-energy uses of fossil fuels is-unfortunately not available in DOE/EIA fuel statistics.

Emissions of  $SF_6$  from aluminum fluxing and degassing have not been estimated. Uncertainties exist as to the quantity of  $SF_6$  used by the aluminum industry and its rate of destruction in its uses as a degassing agent or cover gas.

# **HCFC-22 Production**

Trifluoromethane (HFC-23 or CHF<sub>3</sub>) is generated as a by-product during the manufacture of chlorodifluoromethane (HCFC-22), which is primarily employed in refrigeration and air conditioning systems and as a chemical feedstock for manufacturing synthetic polymers. Since 1990, production and use of HCFC-22 has increased significantly as it has replaced chlorofluorocarbons (CFCs) in many applications. Because HCFC-22 depletes stratospheric ozone, its production for non-feedstock uses is scheduled to be phased out by 2020 under the U.S. Clean Air Act.<sup>21</sup> Feedstock production, in contrast, is permitted to continue indefinitely.

HCFC-22 is produced by the reaction of chloroform (CHCl<sub>3</sub>) and hydrogen fluoride (HF) in the presence of a catalyst, SbCl<sub>5</sub>. The reaction of the catalyst and HF produces  $SbCl_xF_y$ , (where x + y = 5), which reacts with chlorinated hydrocarbons to replace chlorine atoms with fluorine. The HF and chloroform are introduced by submerged piping into a continuous-flow reactor that contains the catalyst in a hydrocarbon mixture of chloroform and partially fluorinated intermediates. The vapors leaving the reactor contain HCFC-21 (CHCl<sub>2</sub>F), HCFC-22 (CHClF<sub>2</sub>), HFC-23 (CHF<sub>3</sub>), HCl, chloroform, and HF. The under-fluorinated intermediates (HCFC-21) and chloroform are then condensed and returned to the reactor, along with residual catalyst, to undergo further fluorination. The final vapors leaving the condenser are primarily HCFC-22, HFC-23, HCl and residual HF. HCl is recovered as a useful byproduct, and the HF is removed. Once separated from HCFC-22, the HFC-23 is generally vented to the atmosphere as an unwanted by-product, or may be captured for use in a limited number of applications.

Emissions of HFC-23 in 1999 were estimated to be  $30.4~\mathrm{Tg~CO_2}$  Eq. (2.6 Gg). This quantity represents a 13 percent decrease from emissions in 1990 (see Table 3-37). Despite a 19 percent increase in production since 1990, the intensity of HFC-23 emissions (the amount of HFC-23 emitted per kilogram of HCFC-22 manufactured) has declined significantly.

In the future, production of HCFC-22 in the United States is expected to decline as non-feedstock HCFC production is phased-out. Feedstock production is anticipated to continue growing, mainly for manufacturing fluorinated polymers. U.S. producers of HCFC-22 are participating in a voluntary program with the EPA to reduce HFC-23 emissions.

## Methodology

The EPA studied the conditions of HFC-23 generation, methods for measuring emissions, and technologies for emissions control. This effort was undertaken in cooperation with the manufacturers of HCFC-22.

The methodology employed for estimating emissions was based upon measurements of critical feed components at individual HCFC-22 production plants. Individual producers also measured HFC-23 concentrations in their output stream by gas chromatography. Using measurements of feed components and HFC-23 concentrations in output streams, the amount of HFC-23 generated was estimated. HFC-23 concentrations were determined at the point the gas leaves the chemical reactor; therefore, estimates also include fugitive emissions.

Table 3-37: HFC-23 Emissions from HCFC-22 Production

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	34.8	3.0
1995	27.1	2.3
1996	31.2	2.7
1997	30.1	2.6
1998	40.0	3.4
1999	30.4	2.6

<sup>&</sup>lt;sup>21</sup> As construed, interpreted, and applied in the terms and conditions of the *Montreal Protocol on Substances that Deplete the Ozone Layer*. [42 U.S.C. §7671m(b), CAA §614]

## **Data Sources**

Emission estimates were provided by the EPA's Climate Protection Division in cooperation with the U.S. manufacturers of HCFC-22.

## **Uncertainty**

A high level of confidence has been attributed to the HFC-23 concentration data employed because measurements were conducted frequently and accounted for day-to-day and process variability. It is estimated that the emissions reported are within 20 percent of the true value. This methodology accounted for the declining intensity of HFC-23 emissions over time. The use of a constant emission factor would not have allowed for such accounting. More simplistic emission estimates generally assume that HFC-23 emissions are between 2 and 4 percent of HCFC-22 production on a mass ratio basis. By 1996, the rate of HFC-23 generated in the United States as a percent of HCFC-22 produced dropped, on average, below 2 percent.

# **Semiconductor Manufacture**

The semiconductor industry uses multiple long-lived fluorinated gases in plasma etching and chemical vapor deposition (CVD) processes. The gases most commonly employed are trifluoromethane (HFC-23), perfluoromethane (CF<sub>4</sub>), perfluoroethane ( $C_2F_6$ ), nitrogen trifluoride (NF<sub>3</sub>), and sulfur hexafluoride (SF<sub>6</sub>), although other compounds such as perfluoropropane ( $C_3F_8$ ) and perfluorocyclobutane (c- $C_4F_8$ ) are also used. The exact combination of compounds is specific to the process employed.

Plasma etching is performed to provide pathways for the conducting material to connect individual circuit components in the silicon, using HFCs, PFCs, SF<sub>6</sub> and other gases in plasma. The etching process creates fluorine atoms that react at the semiconductor surface according to prescribed patterns to selectively remove substrate material. A single semiconductor wafer may require as many as 100 distinct process steps that utilize these gases. Chemical vapor deposition chambers, used for

depositing materials that will act as insulators and wires, are cleaned periodically using PFCs and other gases. During the cleaning cycle the gas is converted to fluorine atoms in plasma, which etches away residual material from chamber walls, electrodes, and chamber hardware. However, due to the low destruction efficiency (high dissociation energy) of PFCs, a portion of the gas flowing into the chamber flows unreacted through the chamber and, unless emission abatement technologies are used, this portion is emitted into the atmosphere. In addition to emissions of unreacted gases, these compounds can also be transformed in the plasma processes into a different HFC or PFC compound, which is then exhausted into the atmosphere. For example, when either CHF<sub>3</sub> or C<sub>2</sub>F<sub>6</sub> is used in cleaning or etching, CF<sub>4</sub> is generated and emitted as a process by-product.

For 1999, it was estimated that total weighted emissions of all fluorinated greenhouse gases by the U.S. semiconductor industry were 6.8 Tg CO<sub>2</sub> Eq. Combined emissions of all fluorinated greenhouse gases are presented in Table 3-38 below. The rapid growth of this industry and the increasing complexity of semiconductor products, which use more PFCs in the production process, led to an increase in emissions of over 130 percent since 1990. However, the growth rate in emissions has slowed since 1997 due in part to an industry slow down and possibly to the initial implementation of PFC emission reduction methods such as process optimization. In the future, emissions are expected to stabilize and ultimately decline over the next decade due to global industry efforts to reduce emissions.

Table 3-38: Emissions of Fluorinated Greenhouse Gases from Semiconductor Manufacture

Year	Tg CO <sub>2</sub> Eq.
1990	2.9
1995	5.5
1996	7.0
1997	7.0
1998	6.8
1999	6.8

Emissions have been estimated using two sets of data. For 1990 through 1994, emissions were estimated based on the historical consumption of silicon (square centimeters), the estimated average number of interconnecting layers in the chips produced, and an estimated per-layer emission factor. (The number of layers per chip, and hence the PFC emissions per square centimeter of silicon, increases as the line-width of the chip decreases.) The average number of layers per chip was based on industry estimates of silicon consumption by line-width and of the number of layers per line-width. The per-layer emission factor was based on the total annual emissions reported by the participants in the PFC Emission Reduction Partnership for the Semiconductor Industry. For the three years for which gas sales data are available (1992 to 1994), the estimates derived using this method are within 10 percent of the estimates derived using gas sales data and average values for emission factors and global warming potentials (GWPs).

For 1995 through 1999, emissions were estimated based on the total annual emissions reported by the participants in the PFC Emission Reduction Partnership for the Semiconductor Industry. Partners estimate their emissions using a range of methods. The partners with relatively high emissions typically multiply estimates of their PFC consumption by process-specific emission factors that they have either measured or obtained from tool suppliers. To estimate total U.S. emissions from semiconductor manufacturing, based on reported partner emissions, a per-plant emission factor was estimated for the partners. This per-plant emission factor was then applied to PFC-using plants operated by semiconductor manufacturers who were not partners, considering the varying characteristics of the plants operated by partners and non-partners (e.g., typical plant size and employed linewidth technology). The resulting estimate of non-partner emissions was added to the emissions reported by the partners to obtain total U.S. emissions.

## **Data Sources**

Aggregate emissions estimates from the semiconductor manufacturers participating in the PFC Emission Reduction Partnership were used to develop the 1995 through 1999 national emission estimate. Estimates of the numbers of plants operated by partners and non-partners, and information on the characteristics of those plants, were derived from the International Fabs on Disk (1999) database. Estimates of silicon consumed by linewidth from 1990 through 1994 were derived from information from VLSI Research (1998), and the number of layers per line-width was obtained from the Semiconductor Industry Association's National Technology Roadmap (1997).

## **Uncertainty**

Emission estimates for this source are improving, but are still relatively uncertain. Emissions vary depending upon the total amount of gas used and the tool and process employed. Much of this information is tracked by semiconductor manufacturers participating in the EPA's PFC Emission Reduction Partnership; however, there is some uncertainty associated with the data collected. In addition, not all semiconductor manufacturers track this information, so when it is extrapolated to total U.S. emissions, the uncertainty related to gas use and emission rates is much greater.

# **Electrical Transmission and Distribution**

The largest use for sulfur hexafluoride (SF<sub>6</sub>), both domestically and internationally, is as an electrical insulator in equipment that transmits and distributes electricity (Science and Policy Associates 1997). The gas has been employed by the electric power industry in the United States since the 1950s because of its dielectric strength and arc-quenching characteristics. It is used in gas-insulated substations, circuit breakers, and other switchgear. Sulfur hexafluoride has replaced flammable insulating oils in many applications and allows for more compact substations in dense urban areas.

Fugitive emissions of SF<sub>6</sub> can escape from gasinsulated substations and switch gear through seals, especially from older equipment. It can also be released during equipment installation and when equipment is opened for servicing, which typically occurs every few years. In the past, some utilities vented SF<sub>6</sub> to the atmosphere during servicing; however, increased awareness and the relatively high cost of the gas have reduced this practice. In the United States, the voluntary partnership—SF<sub>6</sub> Emissions Reduction Partnership for Electric Power Systems—is working with utilities to reduce their emissions and will likely contribute to a reduction of emissions over time.

Emissions of  $SF_6$  from electrical transmission and distribution systems were estimated to be 25.7 Tg  $CO_2$  Eq. (1.1 Gg) in 1999. This quantity amounts to a 25 percent increase over the estimate for 1990 (see Table 3-39).

Table 3-39: SF<sub>6</sub> Emissions from Electrical Transmission and Distribution

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	20.5	0.9
1995	25.7	1.1
1996	25.7	1.1
1997	25.7	1.1
1998	25.7	1.1
1999	25.7	1.1

# Methodology

Emissions of  $SF_6$  were estimated using a top-down, or production-based approach. Specifically, emissions were calculated based upon the following factors: 1) the estimated U.S. production capacity for  $SF_6$ , 2) the estimated use of this production capacity, 3) the fraction of U.S.  $SF_6$  production estimated to be sold annually to fill or refill electrical equipment, and 4) the fraction of these sales estimated to replace emitted gas.

Based on information gathered from chemical manufacturers, it was estimated that in 1994 U.S. production capacity for  $SF_6$  was approximately 3,000 metric tons. It was assumed that plants were operating at 90 percent capacity, which was consistent with industry averages and implied that 2,700 metric tons of  $SF_6$  were produced in 1994. It was further assumed that 75 percent of U.S.  $SF_6$  sales were made to electric utilities and electrical transmission and distribution equipment manufacturers. This assumption is consistent with the estimate—given in Ko, et al. (1993)—that worldwide, 80 percent of  $SF_6$  sales is for electrical transmission and distribution systems. Seventy-five percent of annual U.S. production in 1994 was 2,000 metric tons.

Finally, it was assumed that approximately 50 percent of this production, or 1,000 metric tons, replaced gas emitted into the atmosphere in 1994. This amount is equivalent to 25.7 Tg CO<sub>2</sub> Eq. (when rounding is performed at the end of the calculation). The estimate is based on information showing that emissions rates from electric equipment have been significant and atmospheric measurements indicating that most of the SF<sub>6</sub> produced internationally since the 1950s has been released. Emissions from electrical equipment are known to have occurred from the service and disposal of the equipment and leaks during operation. Leaks from older equipment were reported to release up to 50 percent of the equipment's charge per year, although leaks from newer equipment were reported to release considerably less (e.g., less than 1 percent of the charge per year).

It was assumed that emissions have remained constant at 25.7 Tg  $CO_2$  Eq. since 1995.

## **Data Sources**

Emission estimates were provided by EPA's Climate Protection Division in cooperation with U.S. electric utilities and chemical producers.

# **Uncertainty**

There is currently little verifiable data for estimating  $SF_6$  emissions from electrical transmission and distribution systems. Neither U.S. gas consumption nor emission monitoring data were available. In 1999, the EPA launched a voluntary program to reduce emissions of  $SF_6$  from equipment used to transmit and distribute electricity such as high voltage circuit breakers, substations, transformers, and transmission lines. The EPA anticipates that better information on  $SF_6$  emissions will be available in the future and expects to update  $SF_6$  emission estimates. The updated estimates will be derived from the  $SF_6$  emissions data reported by the Voluntary  $SF_6$  Emissions Reduction Partnership. It is expected that new data will reveal that emissions from electrical transmission and distribution have declined in recent years.

# **Magnesium Production** and **Processing**

The magnesium metal production and casting industry uses sulfur hexafluoride (SF<sub>6</sub>) as a covergas to prevent the violent oxidation of molten magnesium in the presence of air. A dilute gaseous mixture of SF<sub>6</sub> with dry air and/or carbon dioxide is blown over molten magnesium metal to induce and stabilize the formation of a protective crust. A minute portion of the SF<sub>6</sub> reacts with the magnesium to form a thin molecular film of mostly magnesium oxide and some magnesium fluoride. In accordance with current IPCC guidance (IPCC 2000), it is assumed that the amount of SF<sub>6</sub> reacting in magnesium industry application is negligible and thus all SF<sub>6</sub> used is emitted into the atmosphere. Sulfur hexafluoride has been used in this application around the world for the last twenty years. It has largely replaced salt fluxes, sulfur dioxide (SO<sub>2</sub>), and boron trifluoride (BF<sub>3</sub>), which are drastically more toxic and corrosive than SF<sub>6</sub>.

Table 3-40: SF<sub>6</sub> Emissions from Magnesium Production and Processing

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	5.5	0.2
1995	5.5	0.2
1996	5.6	0.2
1997	7.5	0.3
1998	6.3	0.3
1999	6.1	0.3

For 1999, a total of 6.1 Tg  $\rm CO_2$  Eq. (0.3 Gg) of  $\rm SF_6$  was estimated to have been emitted by the magnesium industry (see Table 3-40). There are no significant plans for expansion of primary magnesium production in the United States, but demand for magnesium metal by U.S. casting companies is growing as auto manufacturers design more lightweight magnesium parts into vehicle models. Foreign magnesium producers are expected to meet the growing U.S. demand for primary magnesium.

# Methodology

Emission estimates for the magnesium industry were revised this year to incorporate information provided by EPA's SF<sub>6</sub> Emission Reduction Partnership for the Magnesium Industry. EPA's magnesium industry partner companies represent 100 percent of U.S. primary production and approximately 60 percent of the casting sector. U.S. magnesium metal production (primary and secondary) and consumption data from 1993 to 1999 are available from the U.S. Geological Survey (USGS).<sup>22</sup> Emissions were estimated by multiplying average industry emission factors (kg SF<sub>6</sub>/tonne Mg produced or processed) by the amount of metal produced or consumed in the six major processes that require SF<sub>6</sub> melt protection; 1) primary production, 2) secondary production, 3) die casting, 4) gravity casting, 5) wrought products and, 6) anodes. The emission factors are derived from EPA partner companies' reports, technical publications (Gjestland and Magers 1996), and expert judgement. Although not directly employed, the Norwegian Institute for Air Research (NIAR 1993) has reported a range of emission factors for primary magnesium production as being from 1 to 5 kg of SF<sub>6</sub> per metric tonne of magnesium.

<sup>&</sup>lt;sup>22</sup> http://minerals.usgs.gov/minerals/pubs/commodity/magnesium/index.html#mis

## **Data Sources**

Emission estimates were provided by EPA's Climate Protection Division in cooperation with the U.S. EPA  $SF_6$  Emission Reduction Partnership for the Magnesium Industry and the USGS.

## **Uncertainty**

There are a number of uncertainties in these estimates, including the assumption that  $SF_6$  does not react nor decompose during use. It is possible that the melt surface reactions and high temperatures associated with molten magnesium would cause some gas degradation.

#### Box 3-1: Potential Emission Estimates of HFCs, PFCs, and SF<sub>6</sub>

Emissions of HFCs, PFCs and  $SF_6$  from industrial processes can be estimated in two ways, either as potential emissions or as actual emissions. Emission estimates in this chapter are "actual emissions," which are defined by the *Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories* as estimates that take into account the time lag between consumption and emissions. In contrast, "potential emissions" are defined to be equal to the amount of a chemical consumed in a country, minus the amount of a chemical recovered for destruction or export in the year of consideration. Potential emissions will generally be greater for a given year than actual emissions, since some amount of chemical consumed will be stored in products or equipment and will not be emitted to the atmosphere until a later date, if ever. Because all chemicals consumed will eventually be emitted into the atmosphere, in the long term the cumulative emission estimates using the two approaches should be equivalent unless the chemical is captured and destroyed. Although actual emissions are considered to be the more accurate estimation approach for a single year, estimates of potential emissions are provided for informational purposes.

Separate estimates of potential emissions were not made for industrial processes that fall into the following categories:

- By-product emissions. Some emissions do not result from the consumption or use of a chemical, but are the unintended by-products of another process. For such emissions, which include emissions of CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> from aluminum production and of HFC-23 from HCFC-22 production, the distinction between potential and actual emissions is not relevant.
- Potential emissions that equal actual emissions. For some sources, such as magnesium production and processing, it is assumed
  that there is no delay between consumption and emission and that no destruction of the chemical takes place. It this case, actual
  emissions equal potential emissions.
- Emissions that are not easily defined. In some processes, such as semiconductor manufacture, the gases used in the process
  may be destroyed or transformed into other compounds, which may also be greenhouse gases. It is therefore not logical to
  estimate potential emissions based on consumption of the original chemical.

Table 3-41 presents potential emission estimates for HFCs and PFCs from the substitution of ozone depleting substances and  $SF_6$  emissions from electrical transmission and distribution and other miscellaneous sources such as tennis shoes and sound insulating windows.<sup>23</sup> Potential emissions associated with the substitution for ozone depleting substances were calculated through a combination of the EPA's Vintaging Model and information provided by U.S. chemical manufacturers. For other  $SF_6$  sources, estimates were based on an assumed U.S.  $SF_6$  production capacity and plant utilization to estimate total sales. The portion of this amount used for magnesium processing and assumed to be used for semiconductor manufacture were subtracted.

Table 3-41: 1999 Potential and Actual Emissions of HFCs, PFCs, and  $SF_6$  from Selected Sources (Tg CO<sub>2</sub> Eq.)

Source	Potential	Actual
Substitution of Ozone Depleting Substances	181.4	56.7
Aluminum Production	<del>-</del>	10.0
HCFC-22 Production	<del>-</del>	30.4
Semiconductor Manufacture	<u>-</u>	6.8
Magnesium Production and Processing	6.1	6.1
Other SF <sub>6</sub> Sources*	61.0	25.7
- Not applicable		

Not applicable

<sup>\*</sup>Includes Electrical Transmission and Distribution and, in the case of potential emissions, other miscellaneous sources.

<sup>&</sup>lt;sup>23</sup> See Annex P for a discussion of sources of SF<sub>6</sub> emissions excluded from the actual emissions estimates in this report.

As is the case for other sources of  $SF_6$  emissions, verifiable  $SF_6$  consumption data for magnesium production and processing in United States were not available. Sulfur hexafluoride may also be used as a covergas for the casting of molten aluminum with a high magnesium content; however, it is unknown to what extent this technique is used in the United States.

## **Industrial Sources of Criteria Pollutants**

In addition to the main greenhouse gases addressed above, many industrial processes generate emissions of criteria air pollutants. Total emissions of nitrogen oxides (NO<sub>x</sub>), carbon monoxide (CO), and nonmethane volatile organic compounds (NMVOCs) from non-energy industrial processes from 1990 to 1999 are reported in Table 3-42.

# **Methodology and Data Sources**

The emission estimates for this source were taken directly from the EPA's *National Air Pollutant Emissions Trends*, 1900-1999 (EPA 2000). Emissions were calcu-

lated either for individual categories or for many categories combined, using basic activity data (e.g., the amount of raw material processed) as an indicator of emissions. National activity data were collected for individual categories from various agencies. Depending on the category, these basic activity data may include data on production, fuel deliveries, raw material processed, etc.

Activity data were used in conjunction with emission factors, which together relate the quantity of emissions to the activity. Emission factors are generally available from the EPA's Compilation of Air Pollutant Emission Factors, AP-42 (EPA 1997). The EPA currently derives the overall emission control efficiency of a source category from a variety of information sources, including published reports, the 1985 National Acid Precipitation and Assessment Program emissions inventory, and other EPA databases.

## **Uncertainty**

Uncertainties in these estimates are partly due to the accuracy of the emission factors used and accurate estimates of activity data.

Table 3-42: NO<sub>x</sub>, CO, and NMVOC Emissions from Industrial Processes (Gg)

Gas/Source	1990	1995	1996	1997	1998	1999
NO <sub>x</sub>	921	842	977	992	924	930
Chemical & Allied						
Product Manufacturing	152	144	113	115	117	119
Metals Processing	88	89	75	80	80	80
Storage and Transport	3	5	14	15	15	15
Other Industrial Processes	343	362	397	417	424	426
Miscellaneous*	335	242	377	365	289	290
CO	9,502	5,291	7,227	8,831	5,612	5,604
Chemical & Allied	,	,	,	,	,	,
Product Manufacturing	1,074	1,109	955	972	981	981
Metals Processing	2,395	2,159	1,455	1,550	1,544	1,522
Storage and Transport	69	22	64	64	65	65
Other Industrial Processes	487	566	509	528	535	543
Miscellaneous*	5,479	1,435	4,244	5,716	2,487	2,492
NMVOCs	3,110	2,805	2,354	2,793	2,352	2,281
Chemical & Allied						
Product Manufacturing	575	599	351	352	357	358
Metals Processing	111	113	66	71	71	70
Storage and Transport	1,356	1,499	1,169	1,204	1,204	1,125
Other Industrial Processes	364	409	383	397	402	407
Miscellaneous*	705	185	385	769	318	320

<sup>\*</sup> Miscellaneous includes the following categories: catastrophic/accidental release, other combustion, health services, TSDFs (Transport, Storage, and Disposal Facilities under the Resource Conservation and Recovery Act), cooling towers, and fugitive dust. It does not include agricultural fires or slash/prescribed burning, which are accounted for under the Agricultural Residue Burning source.

Note: Totals may not sum due to independent rounding.